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(54) Title: HARD SURFACE CLEANING COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS (57) Abstract: This invention relates to hard surface cleaning compositions which include mid-chain branched surfactants.		

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HARD SURFACE CLEANING COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS

FIELD OF THE INVENTION

This invention relates to hard surface cleaning products which include mid-chain branched surfactants.

BACKGROUND OF THE INVENTION

The developer and formulator of surfactants for hard surface cleaning must consider a wide variety of possibilities with limited (sometimes inconsistent) information, and then strive to provide overall improvements in one or more of a whole array of criteria, including performance in the presence of free calcium in complex mixtures of surfactants and polymers, e.g. cationic polymers, formulation changes, enzymes, various changes in consumer habits and practices, and the need for biodegradability.

Further, hard surface cleaning should employ materials that enhance the tolerance of the system to hardness, especially to avoid the precipitation of the calcium salts of anionic surfactants. Precipitation of the calcium salts of anionic surfactants is known to cause unsightly deposits on hard surfaces, especially dark hard surfaces. In addition, precipitation of surfactants can lead to losses in performance as a result of the lower level of available cleaning agent. In the context provided by these preliminary remarks, the development of improved alkyl sulfates, alkyl alkoxy sulfates and alkyl alkoxylates for use in hard surface cleaning compositions is clearly a complex challenge. The present invention relates to improvements in such surfactant compositions.

It is an object of the present invention to provide mixtures of the mid-chain branched primary alkyl surfactants which are formulatable with other surfactants to provide cleaning compositions having one or more advantages, including greater product stability at low temperatures, increased resistance to water hardness, greater efficacy in surfactant systems, filming and streaking, improved removal of greasy or particulate body soils, and the like.

BACKGROUND ART

U.S. 3,480,556, EP 439,316, EP 684,300, EP 439,316, U.S. 3,480,556, R.G. Laughlin in "The Aqueous Phase Behavior of Surfactants", Academic Press, N.Y. (1994), Finger et al., "Detergent alcohols - the effect of alcohol structure and molecular weight on surfactant properties", J. Amer. Oil Chemists' Society, Vol. 44, Technical Bulletin, Shell Chemical Co., SC: 364-80, EP 342,917 A, U.S. Patent 4,102,823, GB 1,399,966, G.B. Patent 1,299,966, EP 401,462 A, K.R. Wormuth and S. Zushma, Langmuir, Vol. 7, (1991), pp 2048-2053, R. Varadaraj et al., J. Phys. Chem., Vol. 95, (1991), pp 1671-1676, Varadaraj et al., J. Colloid and Interface Sci., Vol. 140, (1990), pp 31-34, Varadaraj et al., Langmuir, Vol. 6 (1990), pp 1376-1378, U.S. Patent 5,284,989, U.S. 5,026,933, U.S. 4,870,038, Surfactant Science Series, Marcel Dekker, N.Y., CEH Marketing Research Report "Detergent Alcohols" by R.F. Modler et al., Chemical Economics Handbook, 1993, 609.5000 - 609.5002; Kirk Othmer's Encyclopedia of Chemical Technology, 4th Edition, Wiley, N.Y., 1991, "Alcohols, Higher Aliphatic" in Vol. 1, pp 865-913 and references therein.

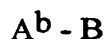
SUMMARY OF THE INVENTION

The present invention provides a hard surface cleaning compositions comprising a mid-chain branched surfactants and a conventional surface cleansing adjuvant.

Specifically, the present invention comprises a hard surface cleaning detergent composition comprising:

- i) from about 0.001% to about 99.9% by weight of a conventional surface cleansing additive; and
- ii) from about 0.1% to about 99.999% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $C_1 - C_3$ alkyl moieties branching from the longest chain,

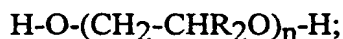
provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})_m\text{OH}$, $(\text{EO/PO})_m\text{OSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

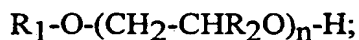
provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5; .

In a second embodiment the present invention also includes a hard surface cleaning composition comprising a branched surfactant system, hereinbefore defined; from about 0.001% to about 20% by weight of an antiresoiling agent selected from the group comprising

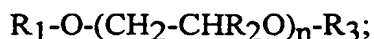
a polyalkoxyethylene glycol according to the formula:



a monocapped polyalkoxyethylene glycol of the formula:



a dicapped polyalkoxyethylene glycol of the formula:



and a mixture thereof, wherein the substituents R_1 and R_3 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms, R_2 is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and wherein n is an integer greater than 0; and from about 0.001% to about 20.0% of a vinylpyrrolidone homopolymer or copolymer.

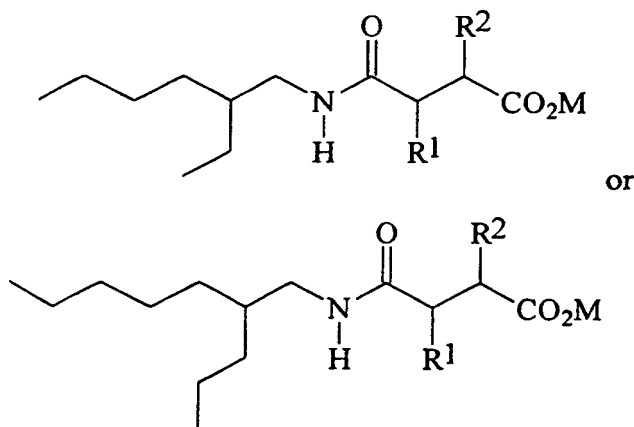
In a third embodiment the present invention also includes a hard surface cleaning composition comprising a branched surfactant system, hereinbefore defined; and from about 0.5% to about 30% by weight of a nonionic surfactant is of the formula



wherein R' is a C_8 to C_{22} alkyl chain or a C_8 to C_{28} alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof;

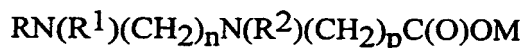
In a fourth embodiment the present invention also includes a hard surface cleaning composition comprising a branched surfactant system, hereinbefore

defined; and from about 0.1% to about 10% by weight of a sulfosuccinamate selected from the group having the formulas:



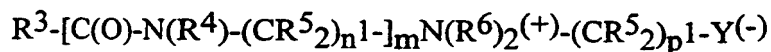
wherein R^1 and R^2 are hydrogen or $-SO_3M^2$ provided R^1 does not equal R^2 ; and M and M^2 are independently hydrogen or a salt forming cation.

In a fifth embodiment the present invention also includes a hard surface cleaning composition comprising a branched surfactant system, hereinbefore defined; from about 0.001% to about 15% amphocarboxylate co-surfactant having the generic formula :



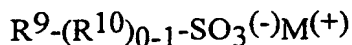
wherein R is a C_6 - C_{10} hydrophobic moiety, including fatty acyl moiety containing from about 6 to about 10 carbon atoms which in combination with the nitrogen atom forms an amido group, R^1 is hydrogen or a C_{1-2} alkyl group, R^2 is a C_{1-2} alkyl, carboxymethoxy ethyl, or hydroxy ethyl, each n is an integer from 1 to 3, each p is an integer from 1 to 2 and M is a water soluble cation selected from alkali metal, ammonium, alkanolammonium, and mixtures thereof cations;

(2) from about 0.02% to about 10% zwitterionic co-surfactant having the generic formula:



wherein each R^3 is an alkyl, or alkylene, group containing from about 10 to about 18 carbon atoms, each (R^4) and (R^6) is selected from the group consisting of hydrogen, methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, each (R^5) is selected from the group consisting of hydrogen and hydroxy groups, with no more than about one hydroxy group in any $(CR^5)_2]_{p^1}$ moiety; m is 0 or 1; each n^1 and p^1 is a number from 1 to about 4; and Y is a carboxylate or sulfonate group; and

(3) from about 0.01% to about 2.0% anionic surfactant having the generic formula:



wherein R^9 is a C_6 - C_{20} alkyl chain; R^{10} is a C_6 - C_{20} alkylene chain, a C_6H_4 phenylene group, or O; and M is the same as before; and

(4) mixtures thereof; and

(iii) from about 0.5% to about 30%, by weight of hydrophobic solvent, having a hydrogen bonding parameter of from about 2 to about 7.7;

(iv) alkaline material to provide a pH, measured on the product, of from about 9 to about 12;

(v) from about 0.01% to about 10% by weight of a substantive polymer that makes glass more hydrophilic, in an effective amount to provide an improvement in spotting/filming after at least three rewettings of the glass, said polymer being selected from the group consisting of polycarboxylate polymer having a molecular weight of from about 10,000 to about 3,000,000 and sulfonated polystyrene polymers having a molecular weight of from about 10,000 to about 1,000,000; and

(vi) from about 0.1 to about 99.99% by weight of an aqueous liquid carrier.

In a sixth embodiment the present invention also includes a hard surface cleaning composition comprising a branched surfactant system, hereinbefore defined; from about 0.1 to about 10% by weight of a zwitterionic co-surfactant; from about 1% to about 10% by weight of a nonionic co-surfactant; from about 1% to about 20% by weight of a hydrophobic solvent; and from about 2% to about 14% by weight of a poly carboxylate builder; wherein said hard surface cleaning composition has a pH of from about 1 to 5.5.

In a seventh embodiment the present invention also includes a method of cleaning a hard surface by administering an effective amount of a hard surface cleaning composition as hereinbefore defined.

In an eighth embodiment the present invention also includes a method for cleaning a hard surface by administering an effective amount of a diluted aqueous solution of the hard surface cleaning compositions as hereinbefore defined.

The invention also comprises a detergent composition containing the branched surfactant mixture, as disclosed herein, in a container in association with instructions to use it with an absorbent structure comprising an effective amount of a superabsorbent material, and, optionally, in a container in a kit comprising the

implement, or, at least, a disposable cleaning pad comprising a superabsorbent material.

The invention also relates to the use of the composition, containing the branched surfactant mixture and a cleaning pad comprising a suberabsorbent material to effect cleaning of soiled surfaces, i.e., the process of cleaning a surface comprising applying an effective amount of a detergent composition containing no more than about 1% detergent surfactant; a level of hydrophobic materials, including solvent, that is less than about 0.5%; and a pH of more than about 7 and absorbing the composition in an absorbent structure comprising a superabsorbent material.

In a ninth embodiment, the present compositions can be used in combination with an implement for cleaning a surface, the implement preferably comprising:

- a. a handle; and
- b. a removable cleaning pad comprising a suberabsorbent material and having a plurality of substantially planar surfaces, wherein each of the substantially planar surfaces contacts the surface being cleaned, and preferably a pad structure which has both a first layer and a second layer, wherein the first layer is located between the scrubbing layer and the second layer and has a smaller width than the second layer.

Depending on the means used for attaching the cleaning pad to the cleaning implement's handle, it may be preferable for the cleaning pad to further comprise a distinct attachment layer. In these embodiments, the absorbent layer would be positioned between the scrubbing layer and the attachment layer.

The detergent composition and, preferably, the implement of the present invention are compatible with all hard surface substrates, including wood, vinyl, linoleum, no wax floors, ceramic, Formica®, porcelain, glass, wall board, and the like.

These and other objects, features and advantages will be apparent from the following description and the appended claims.

All percentages, ratios and proportions herein are on a weight basis unless otherwise indicated. All documents cited herein are hereby incorporated by reference.

DETAILED DESCRIPTION OF THE INVENTION

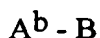
The hard surface cleaning compositions of this invention comprise a surfactant-containing, preferably surfactant-structured liquid phase which comprises a branched surfactant mixture comprising linear and mid-chain branched surfactants. The essential and optional components of the surfactant mixture and other optional

materials of the hard surface cleaning compositions herein, as well as composition form, preparation and use, are described in greater detail as follows: (All concentrations and ratios are on a weight basis unless otherwise specified.)

Specifically, the present invention comprises a hard surface cleaning composition. The hard surface cleaning composition comprises:

- i) from about 0.001% to about 99.9%, by weight of a conventional surface cleansing additive; and
- ii) from about 0.1% to about 99.999% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds less than about 25% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $C_1 - C_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(EO/PO)mOH$, $(EO/PO)mOSO_3M$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5.

The surfactant system will be present in the hard surface cleaning composition at preferably at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, even more preferably still at least about 5%, even more preferably still at least about 8%, most preferably at least about 10%, by weight. Furthermore, the surfactant system will be present in the hard surface cleaning

composition at preferably at less than about 90%, more preferably less than about 75%, even more preferably less than about 50%, even more preferably less than about 35%, even more preferably less than about 20%, most preferably less than about 15%, by weight.

A^b moiety has from about 8 to about 18, preferably from about 9 to about 17, most preferably about 9 to about 15 carbon atoms. The average total number of carbon atoms in the A^b moiety in the branched surfactant mixture defined above should be within the range of greater than about 9 to 14.5, preferably greater than about 9 to about 14, more preferably greater than about 9 to about 13. It is also possible for the average total number of carbon atoms in the A^b moiety, as defined above, to be in the range of about 9 or greater to about 12. The "total" number of carbon atoms as used herein is intended to mean the number of carbon atoms in the longest chain, i.e. the backbone of the molecule, plus the number of carbon atoms in all of the short chains, i.e. the branches.

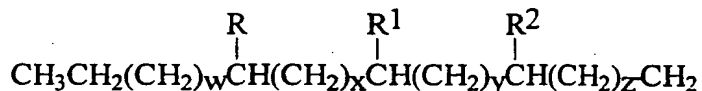
The hard surface cleaning compositions defined herein also comprise from about 0.001% to 99.9% by weight of the composition of a conventional surface cleansing additive.

The conventional surface cleansing additive will be present in the hard surface cleaning composition at preferably at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, even more preferably still at least about 5%, even more preferably still at least about 8%, most preferably at least about 10%, by weight. Furthermore, the conventional surface cleansing additive will be present in the hard surface cleaning composition at preferably at less than about 90%, more preferably less than about 75%, even more preferably less than about 50%, even more preferably less than about 35%, even more preferably less than about 20%, most preferably less than about 15%, by weight. This conventional surface cleansing additive is selected from the group comprising builders, bleaching compounds, aqueous liquid carrier, co-solvents, polymeric additives, pH adjusting materials, hydrotropes, co-surfactants and mixtures thereof, all of which are hereinafter defined.

As used herein, "hard surfaces", typically refers to floors, walls, windows, kitchen and bathroom furniture, appliances and dishes.

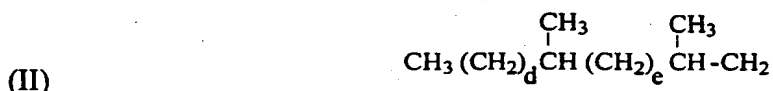
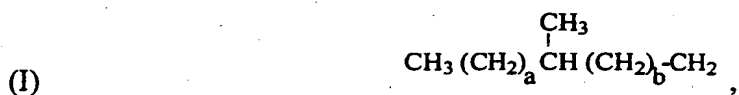
The linear surfactant compounds present in the branched surfactant mixture comprise greater than 25% and less than about 70%, preferably greater than 25% and less than about 60%, more preferably greater than 25% and less than about 50%, by weight of the surfactant mixture.

The branched surfactants for use in the hard surface cleaning compositions of the present invention can preferably comprise compounds of the above formula wherein the A^b moiety is a branched alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched alkyl moiety of this formula, including the R, R¹, and R² branching, is from 8 to 18; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, preferably methyl, provided R, R¹, and R² are not all hydrogen and, when z is 0, at least R or R¹ is not hydrogen; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10 and w + x + y + z is from 2 to 10.

Moreover, an especially preferred branched surfactant for use in the hard surface cleaning compositions of the present invention comprises an A^b moiety which is characterized as having one of the two formulas below and mixtures thereof:



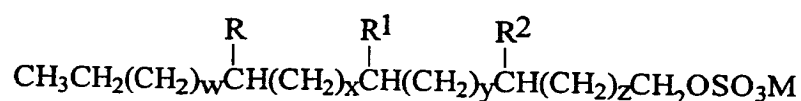
or mixtures thereof; wherein a, b, d, and e are integers, a+b is from 5 to 13, d+e is from 3 to 11 and wherein further

when a + b = 5, a is an integer from 2 to 4 and b is an integer from 1 to 3;
 when a + b = 6, a is an integer from 2 to 5 and b is an integer from 1 to 4;
 when a + b = 7, a is an integer from 2 to 6 and b is an integer from 1 to 5;
 when a + b = 8, a is an integer from 2 to 7 and b is an integer from 1 to 6;
 when a + b = 9, a is an integer from 2 to 8 and b is an integer from 1 to 7;
 when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
 when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
 when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
 when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
 when d + e = 4, d is 2 and e is 1;
 when d + e = 5, d is an integer from 2 to 3 and e is an integer from 1 to 2;
 when d + e = 6, d is an integer from 2 to 4 and e is an integer from 1 to 3;
 when d + e = 7, d is an integer from 2 to 5 and e is an integer from 1 to 4;

when $d + e = 7$, d is an integer from 2 to 6 and e is an integer from 1 to 5;
 when $d + e = 8$, d is an integer from 2 to 7 and e is an integer from 1 to 6;
 when $d + e = 9$, d is an integer from 2 to 8 and e is an integer from 1 to 7;
 when $d + e = 10$, d is an integer from 2 to 9 and e is an integer from 1 to 8.
 when $d + e = 11$, d is an integer from 2 to 10 and e is an integer from 1 to 9.

(1) Mid-chain Branched Primary Alkyl Sulfate Surfactants

The mid-chain branched surfactant system for use in the hard surface cleaning compositions of the present invention may comprise one or more mid-chain branched primary alkyl sulfate surfactants having the formula:



More specifically, the branched surfactant mixtures of the present invention comprise molecules having a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom). These alkyl chain backbones comprise from about 7 to about 17 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from about 9 to 14.5. Thus, the present invention mixtures comprise at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 7 carbon atoms or more than 17 carbon atoms, and the average total number of carbon atoms for the branched primary alkyl chains is within the range of from about 9 to 14.5, preferably greater than about 9 to about 14 and most preferably greater than about 9 to about 13.

For example, a C14 total carbon primary alkyl sulfate surfactant having 11 carbon atoms in the backbone must have 1, 2, or 3 branching units (i.e., R , R^1 and/or R^2) whereby total number of carbon atoms in the molecule is 14. In this example, the C14 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

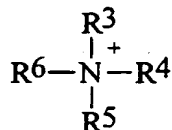
R , R^1 , and R^2 are each independently selected from hydrogen and C_1 - C_3 alkyl (preferably hydrogen or C_1 - C_2 alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R , R^1 , and R^2 are not all hydrogen. Further, when z is 0, at least R or R^1 is not hydrogen.

Although for the purposes of the present invention the surfactant systems of the above formula do not include molecules wherein the units R , R^1 , and R^2 are all

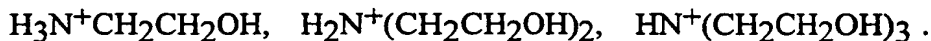
hydrogen (i.e., linear non-branched primary alkyl sulfates), it is to be recognized that the present surfactant systems may still further comprise some amount of linear, non-branched primary alkyl sulfate. Further, this linear non-branched primary alkyl sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite one or more mid-chain branched primary alkyl sulfates according to the present invention, or for purposes of formulating hard surface cleaning compositions some amount of linear non-branched primary alkyl sulfate may be admixed into the final product formulation.

Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol may comprise some amount of the present surfactant system. Such materials may be present as the result of incomplete sulfation of the alcohol used to prepare the alkyl sulfate surfactant, or these alcohols may be separately added to the present hard surface cleaning compositions along with a mid-chain branched alkyl sulfate surfactant according to the present invention.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula



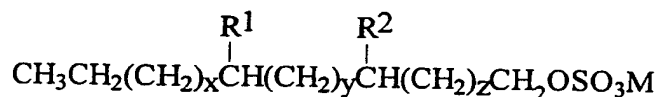
wherein R^3 , R^4 , R^5 and R^6 are independently hydrogen, C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_6 alkanol, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene, and mixtures thereof. Preferred cations are ammonium (R^3 , R^4 , R^5 and R^6 equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R^3 equal to C_1 - C_6 alkanol, R^4 , R^5 and R^6 equal to hydrogen; dialkanol ammonium compounds of the present invention have R^3 and R^4 equal to C_1 - C_6 alkanol, R^5 and R^6 equal to hydrogen; trialkanol ammonium compounds of the present invention have R^3 , R^4 and R^5 equal to C_1 - C_6 alkanol, R^6 equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:



Preferred M is sodium, potassium and the C_2 alkanol ammonium salts listed above; the most M preferred is sodium.

Further regarding the above formula, w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is an integer from 2 to 10.

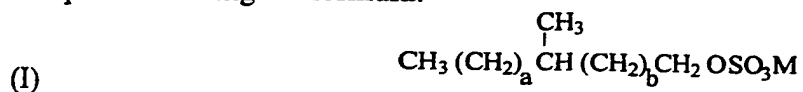
The preferred surfactant system will be present in the hard surface cleaning composition at preferably at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, even more preferably still at least about 5%, even more preferably still at least about 8%, most preferably at least about 10%, by weight. Furthermore, the preferred surfactant mixture will be present in the hard surface cleaning composition at preferably at less than about 45%, more preferably less than about 40%, even more preferably less than about 35%, even more preferably less than about 30%, by weight.

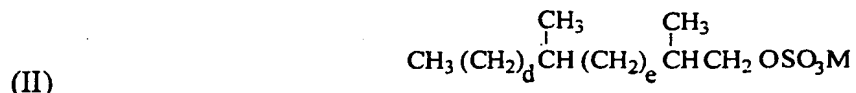


wherein the total number of carbon atoms, including branching, is from 8 to 16, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 9 to about 14; R¹ and R² are each independently hydrogen or C₁-C₃ alkyl; M is a water soluble cation; x is from 0 to 10; y is from 0 to 10; z is from 0 to 10 and x + y + z is from 2 to 10; provided R¹ and R² are not both hydrogen. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkyl sulfates wherein x + y is equal to 6 and z is at least 1.

Preferably, the mixtures of surfactant comprise at least 5% of a mid chain branched primary alkyl sulfate having R¹ and R² independently hydrogen, methyl, provided R¹ and R² are not both hydrogen; x + y is equal to 5, 6 or 7 and z is at least 1. More preferably the mixtures of surfactant comprise at least 20% of a mid chain branched primary alkyl sulfate having R¹ and R² independently hydrogen or methyl, provided R¹ and R² are not both hydrogen; x + y is equal to 5, 6 or 7 and z is at least 1.

Preferred mid-chain branched primary alkyl sulfate surfactants for use in the hard surface cleaning compositions defined herein are selected from the group of compounds having the formula:



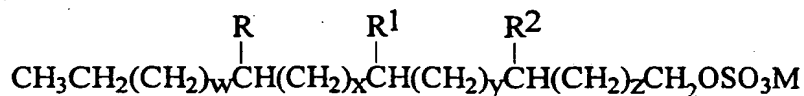


and mixtures thereof; wherein M represents one or more cations; and mixtures thereof; wherein a, b, d, and e are integers, a+b is from 5 to 13, d+e is from 3 to 11 and wherein further

- when a + b = 5, a is an integer from 2 to 4 and b is an integer from 1 to 3;
- when a + b = 6, a is an integer from 2 to 5 and b is an integer from 1 to 4;
- when a + b = 7, a is an integer from 2 to 6 and b is an integer from 1 to 5;
- when a + b = 8, a is an integer from 2 to 7 and b is an integer from 1 to 6;
- when a + b = 9, a is an integer from 2 to 8 and b is an integer from 1 to 7;
- when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
- when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
- when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
- when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
- when d + e = 3, d is 2 and e is 1;
- when d + e = 4, d is an integer from 2 to 3 and e is an integer from 1 to 2;
- when d + e = 5, d is an integer from 2 to 4 and e is an integer from 1 to 3;
- when d + e = 6, d is an integer from 2 to 5 and e is an integer from 1 to 4;
- when d + e = 7, d is an integer from 2 to 6 and e is an integer from 1 to 5;
- when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;
- when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;
- when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8.
- when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9.

Wherein the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of from about 9 to 14.5. Especially preferred mid-chain branched surfactants are those comprising a mixture of compounds having the general formulas from Groups I and II, wherein the molar ratio of compounds according to Group I to Group II is greater than about 4:1, preferably greater than about 9:1 and most preferably greater than about 20:1.

Further, the present surfactant systems may comprise a mixture of linear and branched surfactants wherein the branched primary alkyl sulfates have the formula



wherein the total number of carbon atoms per molecule, including branching, is from 8 to 18, and wherein further for this surfactant mixture the average total number of

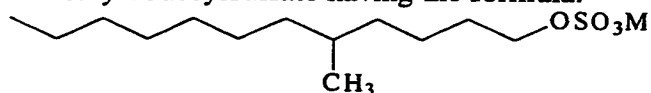
carbon atoms in the branched primary alkyl moieties having the above formula is within the range of from about 9 to 14.5; R , R^1 , and R^2 are each independently selected from hydrogen and C_1 - C_3 alkyl, provided R , R^1 , and R^2 are not all hydrogen; M is a water soluble cation; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and $w + x + y + z$ is from 2 to 10; provided that when R^2 is a C_1 - C_3 alkyl the ratio of surfactants having z equal to 0 to surfactants having z of 1 or greater is at least about 1:1, preferably at least about 1:5, more preferably at least about 1:10, and most preferably at least about 1:20. Also preferred are surfactant compositions, when R^2 is a C_1 - C_3 alkyl, comprising less than about 20%, preferably less than 10%, more preferably less than 5%, most preferably less than 1%, of branched primary alkyl sulfates having the above formula wherein z equals 0.

Preferred mono methyl branched primary alkyl sulfates selected from the group consisting of: 3-methyl undecanol sulfate, 4-methyl undecanol sulfate, 5-methyl undecanol sulfate, 6-methyl undecanol sulfate, 7-methyl undecanol sulfate, 8-methyl undecanol sulfate, 9-methyl undecanol sulfate, 3-methyl dodecanol sulfate, 4-methyl dodecanol sulfate, 5-methyl dodecanol sulfate, 6-methyl dodecanol sulfate, 7-methyl dodecanol sulfate, 8-methyl dodecanol sulfate, 9-methyl dodecanol sulfate, 10-methyl dodecanol sulfate, 3-methyl tridecanol sulfate, 4-methyl tridecanol sulfate, 5-methyl tridecanol sulfate, 6-methyl tridecanol sulfate, 7-methyl tridecanol sulfate, 8-methyl tridecanol sulfate, 9-methyl tridecanol sulfate, 10-methyl tridecanol sulfate, 11-methyl tridecanol sulfate, and mixtures thereof.

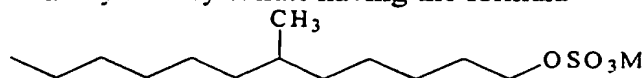
Preferred dimethyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-dimethyl undecanol sulfate, 2,4-dimethyl undecanol sulfate, 2,5-dimethyl undecanol sulfate, 2,6-dimethyl undecanol sulfate, 2,7-dimethyl undecanol sulfate, 2,8-dimethyl undecanol sulfate, 2,9-dimethyl undecanol sulfate, 2,3-dimethyl dodecanol sulfate, 2,4-dimethyl dodecanol sulfate, 2,5-dimethyl dodecanol sulfate, 2,6-dimethyl dodecanol sulfate, 2,7-dimethyl dodecanol sulfate, 2,8-dimethyl dodecanol sulfate, 2,9-dimethyl dodecanol sulfate, 2,10-dimethyl dodecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 13 carbon atoms and having one branching unit are examples of preferred branched surfactants useful in the present invention compositions:

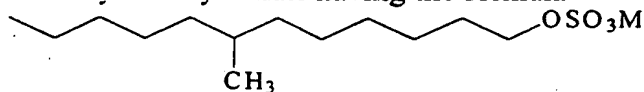
5-methyldodecylsulfate having the formula:



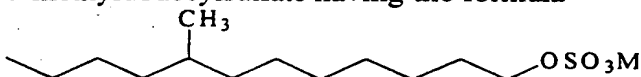
6-methyldodecylsulfate having the formula



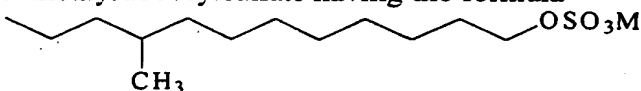
7-methyldodecylsulfate having the formula



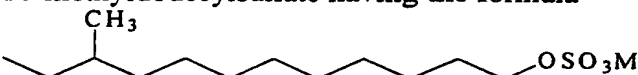
8-methyldodecylsulfate having the formula



9-methyldodecylsulfate having the formula



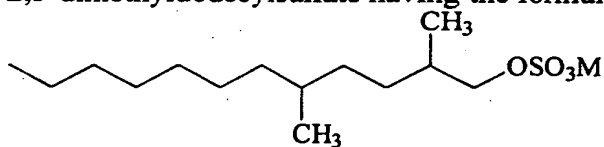
10-methyldodecylsulfate having the formula



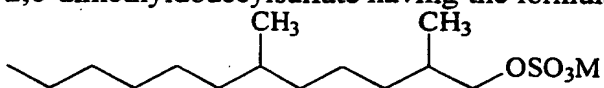
wherein M is preferably sodium.

The following branched primary alkyl sulfates comprising 14 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:

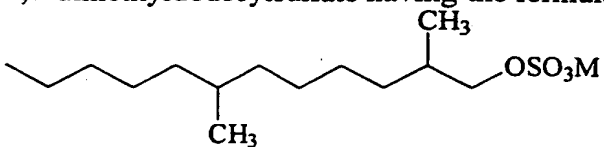
2,5-dimethyldodecylsulfate having the formula:



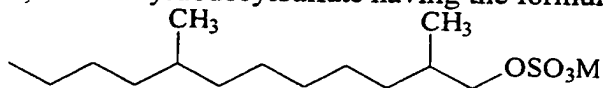
2,6-dimethyldodecylsulfate having the formula



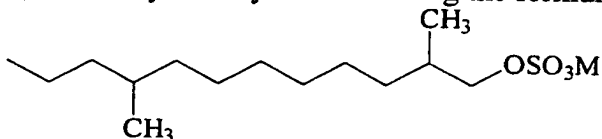
2,7-dimethyldodecylsulfate having the formula



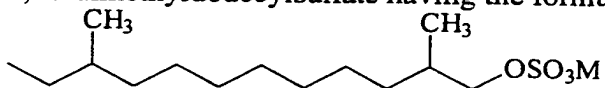
2,8-dimethyldodecylsulfate having the formula



2,9-dimethyldodecylsulfate having the formula



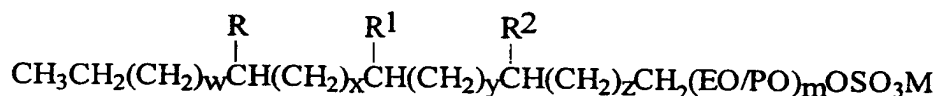
2,10-dimethyldodecylsulfate having the formula



wherein M is preferably sodium.

(2) Mid-chain Branched Primary Alkyl Alkoxylated Sulfate Surfactants

The mid-chain branched surfactant system for use in the hard surface cleaning compositions of the present invention may comprise one or more (preferably a mixture of two or more) mid-chain branched primary alkyl alkoxylated sulfates having the formula:



The surfactant mixtures of the present invention comprise molecules having a linear primary alkoxylated sulfate chain backbone (i.e., the longest linear carbon chain which includes the alkoxy-sulfated carbon atom). These alkyl chain backbones comprise from about 7 to about 17 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties of less than 14.5, preferably within the range of from about 9 to 14.5. Thus, the present invention mixtures comprise at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 7 carbon atoms or more than 17 carbon atoms, and the average total number of carbon atoms for the branched primary alkyl chains is within the range of from about 9 to 14.5, preferably greater than about 9 to about 14 and most preferably greater than about 9 to about 13.

For example, a C14 total carbon primary alkyl sulfate surfactant having 11 carbon atoms in the backbone must have 1, 2, or 3 branching units (i.e., R, R¹ and/or R²) whereby total number of carbon atoms in the alkyl moiety is 14. In this example, the C14 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl (preferably hydrogen or C₁-C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R¹, and R² are not all hydrogen. Further, when z is 0, at least R or R¹ is not hydrogen.

Although for the purposes of the present invention the surfactant systems according to the above formula do not include molecules wherein the units R, R¹, and R² are all hydrogen (i.e., linear non-branched primary alkoxyated sulfates), it is to be recognized that the present surfactant system may still further comprise some amount of linear, non-branched primary alkoxyated sulfate. Further, this linear non-branched primary alkoxyated sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary alkoxyated sulfates according to the present invention, or for purposes of formulating hard surface cleaning compositions some amount of linear non-branched primary alkoxyated sulfate may be admixed into the final product formulation.

It is also to be recognized that some amount of mid-chain branched alkyl sulfate may be present in the surfactant system. This is typically the result of sulfation of non-alkoxyated alcohol remaining following incomplete alkoxylation of the mid-chain branched alcohol used to prepare the alkoxyated sulfate useful herein. It is to be recognized, however, that separate addition of such mid-chain branched alkyl sulfates is also contemplated by the present hard surface cleaning compositions.

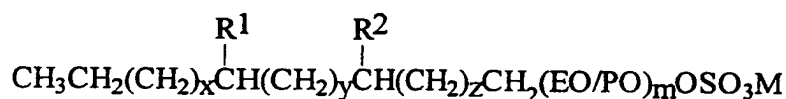
Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol (including polyoxyalkylene alcohols) may comprise some amount of the present invention alkoxyated sulfate-containing compositions. Such materials may be present as the result of incomplete sulfation of the alcohol (alkoxyated or non-alkoxyated) used to prepare the alkoxyated sulfate surfactant, or these alcohols may be separately added to the present hard surface cleaning compositions along with a mid-chain branched alkoxyated sulfate surfactant according to the present invention.

M is as described hereinbefore.

Further regarding the above formula, w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is an integer from 2 to 10.

EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. The (EO/PO)_m moiety may be either a distribution with average degree of alkoxylation (e.g., ethoxylation and/or propoxylation) corresponding to m, or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to m.

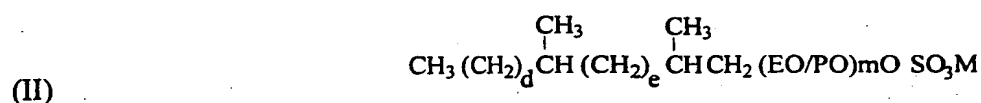
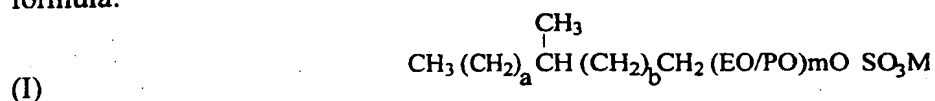
The preferred surfactant system will be present in the hard surface cleaning composition at preferably at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, even more preferably still at least about 5%, even more preferably still at least about 8%, most preferably at least about 10%, by weight. Furthermore, the preferred surfactant mixture will be present in the hard surface cleaning composition at preferably at less than about 45%, more preferably less than about 40%, even more preferably less than about 35%, even more preferably less than about 30%, by weight of the mixture one or more branched primary alkyl alkoxyated sulfates having the formula



wherein the total number of carbon atoms, including branching, is from 8 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 9 to about 14; R¹ and R² are each independently hydrogen or C₁-C₃ alkyl; M is a water soluble cation; x is from 0 to 10; y is from 0 to 10; z is from 0 to 10 and x + y + z is from 2 to 10; provided R¹ and R² are not both hydrogen and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkyl alkoxy sulfates wherein x + y is equal to 6 and z is at least 1.

Preferably, the mixtures of surfactant comprise at least 5% of a mid chain branched primary alkyl sulfate having R^1 and R^2 independently hydrogen, methyl, provided R^1 and R^2 are not both hydrogen; $x + y$ is equal to 5, 6 or 7 and z is at least 1. More preferably the mixtures of surfactant comprise at least 20% of a mid chain branched primary alkyl sulfate having R^1 and R^2 independently hydrogen or methyl, provided R^1 and R^2 are not both hydrogen; $x + y$ is equal to 5, 6 or 7 and z is at least 1.

Preferred mixtures of mid-chain branched primary alkyl alkoxyated sulfate and linear alkyl alkoxyated sulfate surfactants comprise at least about 5 % by weight of one or more mid-chain branched alkyl alkoxyated sulfates having the formula:

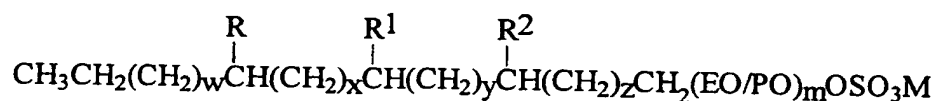


and mixtures thereof. M represents one or more cations. a , b , d , and e are integers, $a+b$ is from 5 to 13, $d+e$ is from 3 to 11 and wherein further

- when $a + b = 5$, a is an integer from 2 to 4 and b is an integer from 1 to 3;
- when $a + b = 6$, a is an integer from 2 to 5 and b is an integer from 1 to 4;
- when $a + b = 7$, a is an integer from 2 to 6 and b is an integer from 1 to 5;
- when $a + b = 8$, a is an integer from 2 to 7 and b is an integer from 1 to 6;
- when $a + b = 9$, a is an integer from 2 to 8 and b is an integer from 1 to 7;
- when $a + b = 10$, a is an integer from 2 to 9 and b is an integer from 1 to 8;
- when $a + b = 11$, a is an integer from 2 to 10 and b is an integer from 1 to 9;
- when $a + b = 12$, a is an integer from 2 to 11 and b is an integer from 1 to 10;
- when $a + b = 13$, a is an integer from 2 to 12 and b is an integer from 1 to 11;
- when $d + e = 3$, d is 2 and e is 1;
- when $d + e = 4$, d is an integer from 2 to 3 and e is an integer from 1 to 2;
- when $d + e = 5$, d is an integer from 2 to 4 and e is an integer from 1 to 3;
- when $d + e = 6$, d is an integer from 2 to 5 and e is an integer from 1 to 4;
- when $d + e = 7$, d is an integer from 2 to 6 and e is an integer from 1 to 5;
- when $d + e = 8$, d is an integer from 2 to 7 and e is an integer from 1 to 6;
- when $d + e = 9$, d is an integer from 2 to 8 and e is an integer from 1 to 7;
- when $d + e = 10$, d is an integer from 2 to 9 and e is an integer from 1 to 8;
- when $d + e = 11$, d is an integer from 2 to 10 and e is an integer from 1 to 9.

The average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of from about 9 to 14.5 and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. Especially preferred mid-chain branched surfactants are those comprising a mixture of compounds having the general formulas from Groups I and II, wherein the molar ratio of compounds according to Group I to Group II is greater than about 4:1, preferably greater than about 9:1 and most preferably greater than about 20:1

Further, the present surfactant systems may comprise a mixture of linear and branched surfactants wherein the branched primary alkyl alkoxylated sulfates has the formula:



wherein the total number of carbon atoms per molecule, including branching, is from 8 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of from about 9 to 14.5; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, provided R, R¹, and R² are not all hydrogen; M is a water soluble cation; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is from 2 to 10; EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5; provided that when R² is a C₁-C₃ alkyl the ratio of surfactants having z equal to 1 or greater to surfactants having z of 0 is at least about 1:1, preferably at least about 5:1, more preferably at least about 10:1, and most preferably at least about 20:1. Also preferred are surfactant compositions, when R² is a C₁-C₃ alkyl, comprising less than about 20%, preferably less than 10%, more preferably less than 5%, most preferably less than 1%, of branched primary alkyl alkoxylated sulfate having the above formula wherein z equals 0.

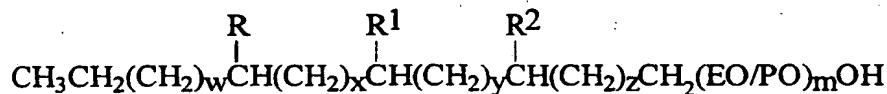
Preferred mono-methyl branched primary alkyl ethoxylated sulfates are selected from the group consisting of: 3-methyl dodecanol ethoxylated sulfate, 4-

methyl dodecanol ethoxylated sulfate, 5-methyl dodecanol ethoxylated sulfate, 6-methyl dodecanol ethoxylated sulfate, 7-methyl dodecanol ethoxylated sulfate, 8-methyl dodecanol ethoxylated sulfate, 9-methyl dodecanol ethoxylated sulfate, 10-methyl dodecanol ethoxylated sulfate, 3-methyl tridecanol ethoxylated sulfate, 4-methyl tridecanol ethoxylated sulfate, 5-methyl tridecanol ethoxylated sulfate, 6-methyl tridecanol ethoxylated sulfate, 7-methyl tridecanol ethoxylated sulfate, 8-methyl tridecanol ethoxylated sulfate, 9-methyl tridecanol ethoxylated sulfate, 10-methyl tridecanol ethoxylated sulfate, 11-methyl tridecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

Preferred dimethyl branched primary alkyl ethoxylated sulfates selected from the group consisting of: 2,3-dimethyl undecanol ethoxylated sulfate, 2,4-dimethyl undecanol ethoxylated sulfate, 2,5-dimethyl undecanol ethoxylated sulfate, 2,6-dimethyl undecanol ethoxylated sulfate, 2,7-dimethyl undecanol ethoxylated sulfate, 2,8-dimethyl undecanol ethoxylated sulfate, 2,9-dimethyl undecanol ethoxylated sulfate, 2,3-dimethyl dodecanol ethoxylated sulfate, 2,4-dimethyl dodecanol ethoxylated sulfate, 2,5-dimethyl dodecanol ethoxylated sulfate, 2,6-dimethyl dodecanol ethoxylated sulfate, 2,7-dimethyl dodecanol ethoxylated sulfate, 2,8-dimethyl dodecanol ethoxylated sulfate, 2,9-dimethyl dodecanol ethoxylated sulfate, 2,10-dimethyl dodecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

(3) Mid-chain Branched Primary Alkyl Polyoxyalkylene Surfactants

The present branched surfactant system for use in the hard surface cleaning compositions may comprise one or more mid-chain branched primary alkyl polyoxyalkylene surfactants having the formula



The surfactant mixtures of the present invention comprise molecules having a linear primary polyoxyalkylene chain backbone (i.e., the longest linear carbon chain which includes the alkoxyated carbon atom). These alkyl chain backbones comprise from 7 to 17 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from greater than

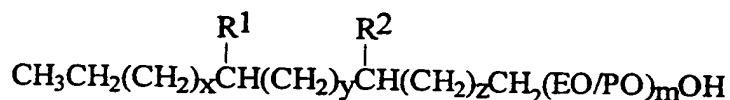
about 9 to 14.5. Thus, the present invention mixtures comprise at least one polyoxyalkylene compound having a longest linear carbon chain of not less than 7 carbon atoms or more than 17 carbon atoms, and the total number of carbon atoms including branching must be at least 8, and further the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than about 9 to 14.5.

For example, a C14 total carbon (in the alkyl chain) primary polyoxyalkylene surfactant having 13 carbon atoms in the backbone must have a methyl branching unit (either R, R¹ or R² is methyl) whereby the total number of carbon atoms in the alkyl moiety is 14.

R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl (preferably hydrogen or C₁-C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R¹, and R² are not all hydrogen. Further, when z is 0, at least R or R¹ is not hydrogen.

Although for the purposes of the present invention the surfactant systems of the above formula do not include molecules wherein the units R, R¹, and R² are all hydrogen (i.e., linear non-branched primary polyoxyalkylenes), it is to be recognized that the present surfactant systems may still further comprise some amount of linear, non-branched primary polyoxyalkylene. Further, this linear non-branched primary polyoxyalkylene surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary polyoxyalkylenes according to the present invention, or for purposes of formulating hard surface cleaning compositions some amount of linear non-branched primary polyoxyalkylene may be admixed into the final product formulation.

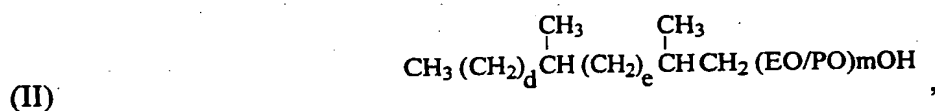
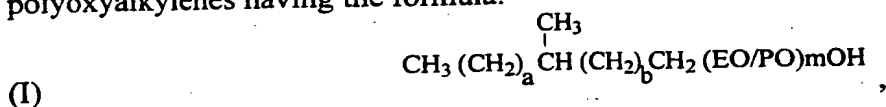
The preferred surfactant system will be present in the hard surface cleaning composition at preferably at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, even more preferably still at least about 5%, even more preferably still at least about 8%, most preferably at least about 10%, by weight. Furthermore, the preferred surfactant mixture will be present in the hard surface cleaning composition at preferably at less than about 45%, more preferably less than about 40%, even more preferably less than about 35%, even more preferably less than about 30%, by weight of the mixture one or more branched primary alkyl polyoxyalkylenes having the formula



wherein the total number of carbon atoms, including branching, is from 8 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 9 to about 14; R^1 and R^2 are each independently hydrogen or C_1 - C_3 alkyl; x is from 0 to 10; y is from 0 to 10; z is at least 1; and $x + y + z$ is from 4 to 10; provided R^1 and R^2 are not both hydrogen; and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, more preferably ethoxy, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary polyoxyalkylenes wherein z is at least 2.

Preferably, the mixtures of surfactant comprise at least 0.5%, preferably at least about 1%, of a mid chain branched primary alkyl polyoxyalkylene having R^1 and R^2 independently hydrogen or methyl, provided R^1 and R^2 are not both hydrogen; $x + y$ is equal to 5, 6 or 7 and z is at least 1.

Preferred hard surface cleaning compositions according to the present invention comprise from about 0.001% to about 99% of a mixture of mid-chain branched primary alkyl polyoxyalkylene surfactants, said mixture comprising at least about 5 % by weight of one or more mid-chain branched alkyl polyoxyalkylenes having the formula:



or mixtures thereof; wherein a , b , d , and e are integers, $a+b$ is from 5 to 13, $d+e$ is from 3 to 11 and wherein further

when $a + b = 5$, a is an integer from 2 to 4 and b is an integer from 1 to 3;
 when $a + b = 6$, a is an integer from 2 to 5 and b is an integer from 1 to 4;
 when $a + b = 7$, a is an integer from 2 to 6 and b is an integer from 1 to 5;
 when $a + b = 8$, a is an integer from 2 to 7 and b is an integer from 1 to 6;
 when $a + b = 9$, a is an integer from 2 to 8 and b is an integer from 1 to 7;
 when $a + b = 10$, a is an integer from 2 to 9 and b is an integer from 1 to 8;
 when $a + b = 11$, a is an integer from 2 to 10 and b is an integer from 1 to 9;
 when $a + b = 12$, a is an integer from 2 to 11 and b is an integer from 1 to 10;
 when $a + b = 13$, a is an integer from 2 to 12 and b is an integer from 1 to 11;

when $d + e = 3$, d is 2 and e is 1;

when $d + e = 4$, d is an integer from 2 to 3 and e is an integer from 1 to 2;

when $d + e = 5$, d is an integer from 2 to 4 and e is an integer from 1 to 3;

when $d + e = 6$, d is an integer from 2 to 5 and e is an integer from 1 to 4;

when $d + e = 7$, d is an integer from 2 to 6 and e is an integer from 1 to 5;

when $d + e = 8$, d is an integer from 2 to 7 and e is an integer from 1 to 6;

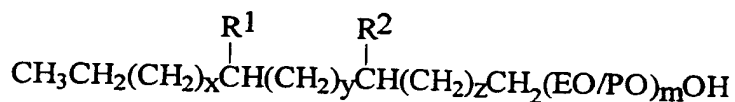
when $d + e = 9$, d is an integer from 2 to 8 and e is an integer from 1 to 7;

when $d + e = 10$, d is an integer from 2 to 9 and e is an integer from 1 to 8.

when $d + e = 11$, d is an integer from 2 to 10 and e is an integer from 1 to 9.

and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than about 9 to 14.5; and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15.

Further, the present surfactant system may comprise a mixture of linear and branched surfactants wherein the branched primary alkyl polyoxyalkylene has the formula:



wherein the total number of carbon atoms per molecule, including branching, is from 8 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of from about 9 to 14.5; R , R^1 , and R^2 are each independently selected from hydrogen and C_1 - C_3 alkyl, provided R , R^1 , and R^2 are not all hydrogen; M is a water soluble cation; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and $w + x + y + z$ is from 2 to 10; EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15; provided that when R^2 is a C_1 - C_3 alkyl the ratio of surfactants having z equal to 1 or greater to surfactants having z of 0 is at least about 1:1, preferably at least about 5:1, more preferably at least about 10:1, and most preferably at least about 20:1. Also preferred are surfactant compositions, when R^2 is a C_1 - C_3 alkyl, comprising less than about 20%,

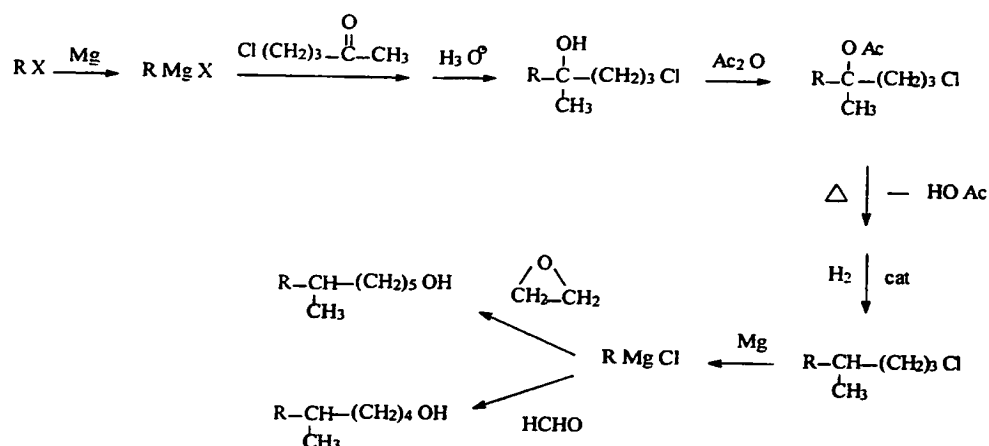
preferably less than 10%, more preferably less than 5%, most preferably less than 1%, of branched primary alkyl polyoxyalkylene having the above formula wherein z equals 0.

Preferred mono-methyl branched primary alkyl ethoxylates are selected from the group consisting of: 3-methyl dodecanol ethoxylate, 4-methyl dodecanol ethoxylate, 5-methyl dodecanol ethoxylate, 6-methyl dodecanol ethoxylate, 7-methyl dodecanol ethoxylate, 8-methyl dodecanol ethoxylate, 9-methyl dodecanol ethoxylate, 10-methyl dodecanol ethoxylate, 3-methyl tridecanol ethoxylate, 4-methyl tridecanol ethoxylate, 5-methyl tridecanol ethoxylate, 6-methyl tridecanol ethoxylate, 7-methyl tridecanol ethoxylate, 8-methyl tridecanol ethoxylate, 9-methyl tridecanol ethoxylate, 10-methyl tridecanol ethoxylate, 11-methyl tridecanol ethoxylate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 5 to about 15.

Preferred dimethyl branched primary alkyl ethoxylates selected from the group consisting of: 2,3-dimethyl undecanol ethoxylate, 2,4-dimethyl undecanol ethoxylate, 2,5-dimethyl undecanol ethoxylate, 2,6-dimethyl undecanol ethoxylate, 2,7-dimethyl undecanol ethoxylate, 2,8-dimethyl undecanol ethoxylate, 2,9-dimethyl undecanol ethoxylate, 2,3-dimethyl dodecanol ethoxylate, 2,4-dimethyl dodecanol ethoxylate, 2,5-dimethyl dodecanol ethoxylate, 2,6-dimethyl dodecanol ethoxylate, 2,7-dimethyl dodecanol ethoxylate, 2,8-dimethyl dodecanol ethoxylate, 2,9-dimethyl dodecanol ethoxylate, 2,10-dimethyl dodecanol ethoxylate and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 5 to about 15.

Preparation of Mid-chain Branched Surfactants

The following reaction scheme outlines a general approach to the preparation of the mid-chain branched primary alcohol useful for alkoxylating and/or sulfating to prepare the mid-chain branched primary alkyl surfactants of the present invention. Linear alcohol can be added to the branched alcohol prior to alkoxylating and/or sulfating.



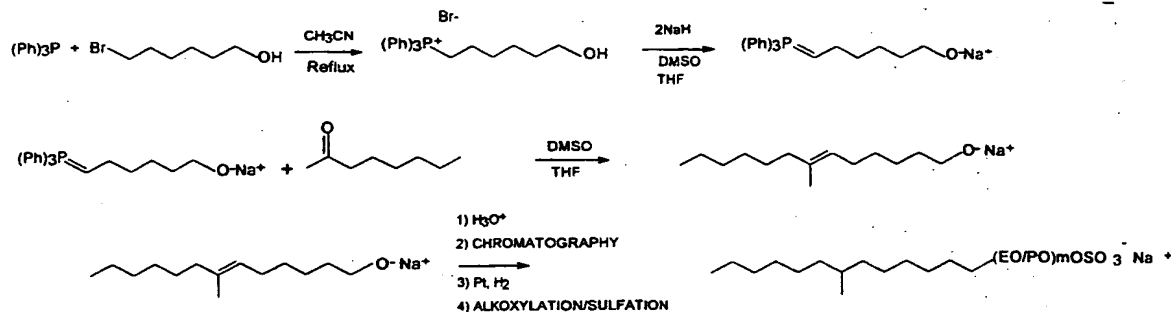
An alkyl halide is converted to a Grignard reagent and the Grignard is reacted with a haloketone. After conventional acid hydrolysis, acetylation and thermal elimination of acetic acid, an intermediate olefin is produced (not shown in the scheme) which is hydrogenated forthwith using any convenient hydrogenation catalyst such as Pd/C.

This route is favorable over others in that the branch, in this illustration a 5-methyl branch, is introduced early in the reaction sequence.

Formulation of the alkyl halide resulting from the first hydrogenation step yields alcohol product, as shown in the scheme. This can be alkoxyated using standard techniques and/or sulfated using any convenient sulfating agent, e.g., chlorosulfonic acid, SO₃/air, or oleum, to yield the final branched primary alkyl surfactant. There is flexibility to extend the branching one additional carbon beyond that which is achieved by a single formulation. Such extension can, for example, be accomplished by reaction with ethylene oxide. See "Grignard Reactions of Nonmetallic Substances", M.S. Kharasch and O. Reinmuth, Prentice-Hall, N.Y., 1954; *J. Org. Chem.*, J. Cason and W. R. Winans, Vol. 15 (1950), pp 139-147; *J. Org. Chem.*, J. Cason et al., Vol. 13 (1948), pp 239-248; *J. Org. Chem.*, J. Cason et al., Vol. 14 (1949), pp 147-154; and *J. Org. Chem.*, J. Cason et al., Vol. 15 (1950), pp 135- 138 all of which are incorporated herein by reference.

In variations of the above procedure, alternate haloketones or Grignard reagents may be used. PBr₃ halogenation of the alcohol from formulation or ethoxylation can be used to accomplish an iterative chain extension.

The preferred mid-chained branched primary alkyl alkoxyated sulfates (as well as the polyoxyalkylenes and alkyl sulfates, by choosing to only alkoxyate or sulfate the intermediate alcohol produced) of the present invention can also be readily prepared as follows:



A conventional bromoalcohol is reacted with triphenylphosphine followed by sodium hydride, suitably in dimethylsulfoxide/tetrahydrofuran, to form a Wittig adduct. The Wittig adduct is reacted with an alpha methyl ketone, forming an internally unsaturated methyl-branched alcoholate. Hydrogenation followed by alkoxylation and/or sulfation yields the desired mid-chain branched primary alkyl surfactant. Although the Wittig approach does not allow the practitioner to extend the hydrocarbon chain, as in the Grignard sequence, the Wittig typically affords higher yields. See *Agricultural and Biological Chemistry*, M. Horiike et al., vol. 42 (1978), pp 1963-1965 included herein by reference.

Any alternative synthetic procedure in accordance with the invention may be used to prepare the branched primary alkyl surfactants. The mid-chain branched primary alkyl surfactants may, in addition be synthesized or formulated in the presence of the conventional homologs, for example linear homologues or any of those which may be formed in an industrial process which produces 2-alkyl branching as a result of hydroformylation.

In certain preferred embodiments of the surfactant mixtures of the present invention, especially those derived from fossil fuel sources involving commercial processes, said surfactant mixtures comprise at least 1 mid-chain branched primary alkyl surfactant, preferably at least 2, more preferably at least 5, most preferably at least 8. Particularly suitable for preparation of certain surfactant mixtures of the present invention are "oxo" reactions wherein a branched chain olefin is subjected to catalytic isomerization and hydroformylation prior to alkoxylation and/or sulfation. The preferred processes resulting in such mixtures utilize fossil fuels as the starting material feedstock. Preferred processes utilize Oxo reaction on olefins (alpha or internal) with a limited amount of branching. Suitable olefins may be made by dimerization of linear alpha or internal olefins, by controlled oligomerization of low molecular weight linear olefins, by skeletal rearrangement of detergent range olefins,

by dehydrogenation/skeletal rearrangement of detergent range paraffins, or by Fischer-Tropsch reaction. These reactions will in general be controlled to:

- 1) give a large proportion of olefins in the desired detergent range (while allowing for the addition of a carbon atom in the subsequent Oxo reaction),
- 2) produce a limited number of branches, preferably mid-chain,
- 3) produce C₁-C₃ branches, more preferably ethyl, most preferably methyl,
- 4) limit or eliminate gem dialkyl branching i.e. to avoid formation of quaternary carbon atoms.

The linear olefin content can be controlled in various ways, e.g., by controlling the extent to which skeletal rearrangement is allowed to proceed or by blending of branched and linear olefins. The suitable olefins can undergo Oxo reaction to give primary alcohols either directly or indirectly through the corresponding aldehydes. That is, the branched surfactant mixture is made from the oxygenated products comprising aldehydes or alcohols produced by subjecting an olefin-rich feedstock to carbon monoxide and hydrogen in the presence of a catalytically effective quantity of hydroformylation catalyst and under hydroformylation reaction conditions. When an internal olefin is used, an Oxo catalyst is normally used which is capable of prior pre-isomerization of internal olefins primarily to alpha olefins. While a separately catalyzed (i.e. non-Oxo) internal to alpha isomerization could be effected, this is optional. On the other hand, if the olefin-forming step itself results directly in an alpha olefin (e.g. with high pressure Fischer-Tropsch olefins of detergent range), then use of a non-isomerizing Oxo catalyst is not only possible, but preferred.

A preferred embodiment of the surfactant mixtures of the present invention involves those materials derived from commercial processes wherein an olefin-rich feedstock containing branched chain olefins, linear olefins and other olefins, e.g., olefins containing cyclical structures, substituted cyclical olefins, and the like, is subjected to carbon monoxide and hydrogen in the presence of a catalytic amount of a hydroformylation catalyst prior to alkoxylation and/or sulfation. In this embodiment, the olefin-rich feedstock is obtained by subjecting a synthesis gas comprising carbon monoxide (CO) and hydrogen (H₂) to Fischer-Tropsch reaction conditions in the presence of an iron-based, a cobalt-based, or an iron/cobalt-based Fischer-Tropsch catalyst. An exemplification of the alcohols and olefin mixtures of this embodiment are those described by WO 97/01521 and in the Sasol Chemical Industries (Pty. Ltd) hereafter referred to as "Sasol", technical product bulletin dated October 1, 1996 entitled SASOL DETERGENT ALCOHOLS, both of which are incorporated herein by reference.

The following examples provide methods for synthesizing various compounds useful in the present invention compositions. The linear content of these surfactant mixtures exemplified are from about 35% to about 45%, unless the amount is specified in the specific example, by weight of surfactant mixture.

EXAMPLE I

Preparation of sodium 7-methyltridecyl ethoxylated (E2) and sulfate

Synthesis of (6-hydroxyhexyl) triphenylphosphonium bromide

Into a 5L, 3 neck round bottom flask fitted with nitrogen inlet, condenser, thermometer, mechanical stirring and nitrogen outlet is added 6-bromo-1-hexanol (500g, 2.76 mol), triphenylphosphine (768g, 2.9mol) and acetonitrile (1800 ml) under nitrogen. The reaction mixture is heated to reflux for 72 hrs. The reaction mixture is cooled to room temperature and transferred into a 5L beaker. The product is recrystallized from anhydrous ethyl ether (1.5L) at 10°C. Vacuum filtration followed by washing with ethyl ether and drying in a vacuum oven at 50°C for 2 hrs. gives 1140g of the desired product as white crystals.

Synthesis of 7- methyltridecene-1-ol

Into a dried 5L, 3 neck round bottom flask fitted with mechanical stirring, nitrogen inlet, dropping funnel, thermometer and nitrogen outlet is added 70.2g of 60% sodium hydride (1.76 mol) in mineral oil. The mineral oil is removed by washing with hexanes. Anhydrous dimethyl sulfoxide (500ml) is added to the flask and the mixture is heated to 70°C until evolution of hydrogen stops. The reaction mixture is cooled to room temperature followed by addition of 1L of anhydrous tetrahydrofuran. (6-hydroxyhexyl) triphenylphosphonium bromide (443.4g, 1 mol) is slurried with warm anhydrous dimethyl sulfoxide (50°C, 500ml) and slowly added to the reaction mixture through the dropping funnel while keeping it at 25-30°C. The mixture is stirred for 30 minutes at room temperature at which time 2-octanone (140.8g, 1.1 mol) is slowly added through a dropping funnel. Reaction is slightly exothermic and cooling is needed to maintain 25-30°C. The mixture is stirred for 18 hr. and then poured into a 5L beaker containing 1L purified water with stirring. The oil phase (top) is allowed to separate out in a separatory funnel and the water phase is removed. The water phase is washed with hexanes (500ml) and the organic phase is separated and combined with the oil phase from the water wash. The organic mixture is then extracted with water 3 times (500ml each) followed by vacuum distillation to collect the clear, oily product (110g) at 140C and 1mm Hg.

Hydrogenation of 7-methyltridecene-1-ol

Into a 3L rocking autoclave liner is added 7-methyltridecene-1-ol (108g, 0.508mol), methanol (300ml) and platinum on carbon (10% by weight, 35g). The mixture is hydrogenated at 180°C under 1200 psig of hydrogen for 13 hrs., cooled and vacuum filtered through Celite 545 with washing of the Celite 545, suitably with methylene chloride. If needed, the filtration can be repeated to eliminate traces of Pt catalyst, and magnesium sulfate can be used to dry the product. The solution of product is concentrated on a rotary evaporator to obtain a clear oil (104g).

Alkoxylation of 7-methyltridecanol

Into a dried 1L 3 neck round bottom flask fitted with a nitrogen inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added the alcohol from the preceding step. For purposes of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 80-100° C. Continuing with a nitrogen sweep, sodium metal is added as the catalyst and allowed to melt with stirring at 120-140° C. With vigorous stirring, ethylene oxide gas is added in 140 minutes while keeping the reaction temperature at 120-140° C. After the correct weight (equal to two equivalents of ethylene oxide) has been added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The desired 7-methyltridecyl ethoxylate (average of 2 ethoxylates per molecule) product is then collected. The 7-methyl tridecyl ethoxylate is blended with n-tetradecanol ethoxylate (E2) to yield a composition containing at least 25% linear alcohol.

Sulfation of 7-methyltridecyl and n-tetradecanol ethoxylate (E2)

Into a dried 1L 3 neck round bottom flask fitted with a nitrogen inlet, dropping funnel, thermometer, mechanical stirring and nitrogen outlet is added chloroform and the blend of 7-methyltridecyl ethoxylate (E2) and n-tetradecanol ethoxylate (E2) from the preceding step. Chlorosulfonic acid is slowly added to the stirred mixture while maintaining 25-30°C temperature with an ice bath. Once HCl evolution has stopped slowly add sodium methoxide (25% in methanol) while keeping temperature at 25-30°C until a aliquot at 5% concentration in water maintains a pH of 10.5. To the mixture is added hot ethanol (55°C) and vacuum filtered immediately. The filtrate is concentrated to a slurry on a rotary evaporator, cooled and then poured into ethyl ether. The mixture is chilled to 5°C and vacuum

filtered to provide the desired blend of 7-methyltridecyl / n-tetradecyl ethoxylate (average of 2 ethoxylates per molecule) sulfate, sodium salt, product.

EXAMPLE II

Preparation of mid-chain branched C12,13 and C14,15 sodium alcohol sulfate, alcohol ethoxylate, and sodium alcohol ethoxy sulfate from Sasol alcohol samples.

Alcohol samples were received from Sasol and had been prepared by hydroformylation of alpha olefins produced by a Fischer Tropsch process as described in Patent WO 97/01521 and according to the Sasol R&D technical product bulletin dated October 1, 1996 entitled SASOL DETERGENT ALCOHOLS. Sodium alkyl sulfates, alcohol ethoxylates and sodium alkyl ethoxy sulfates were synthesized from both the C12,13 and C14,15 alcohols.

Sulfation of Sasol C12,13 Alcohol

Into a dried 2L 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Alcohol (234.0 g, 1.2 mol) and diethyl ether (250 ml). Chlorosulfonic acid (146.8 g, 1.26 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum is increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (285.1 g, 1.32 mol) and methanol (600ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 321g of yellow tacky solid, the cat SO₃ analysis shows the sample is about 93% active. The pH of the sample is about 9.5.

Ethoxylation of Sasol C12,13 Alcohol to E3

Into a dried 1L 3 neck round bottom flask fitted with a gas inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Alcohol (195.0 g, 1.0 mol). For the purpose of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 60-80°C. Continuing

with a nitrogen sweep, sodium metal (1.2 g, 0.05 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (132.0 g, 3.0 mol) is added in 180 minutes while keeping the reaction temperature 120-140°C. After the correct weight of ethylene oxide is added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The gold liquid product (323.0 g, 0.988 mol) is bottled under nitrogen.

Sulfation of Sasol C12,13 Alcohol Ethoxylate (E3)

Into a dried 2L 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Ethoxylate (E3) (261.6 g, 0.8 mol) and diethyl ether (300 ml). Chlorosulfonic acid (97.9 g, 0.84 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum is increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (190.1 g, 0.88 mol) and methanol (400ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 304 g of yellow tacky solid, the cat SO₃ analysis shows the sample is about 95% active. The pH of the sample is about 10.1.

Sulfation of Sasol C14,15 Alcohol

Into a dried 500 ml 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C14,15 Alcohol (87.2 g, 0.4 mol) and diethyl ether (150 ml). Chlorosulfonic acid (48.9 g, 0.42 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum is increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (95.0 g,

0.44 mol) and methanol (300ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 108g of yellow tacky solid, the cat SO₃ analysis shows the sample is about 89% active. The pH of the sample is about 9.8.

Ethoxylation of Sasol C14.15 Alcohol to E2.5

Into a dried 1L 3 neck round bottom flask fitted with a gas inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C14,15 Alcohol (218.0 g, 1.0 mol). For the purpose of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 60-80°C. Continuing with a nitrogen sweep, sodium metal (1.2 g, 0.05 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (110.0 g, 2.5 mol) is added in 140 minutes while keeping the reaction temperature 120-140°C. After the correct weight of ethylene oxide is added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The amber liquid product (323.1 g, 0.985 mol) is bottled under nitrogen.

Sulfation of Sasol C14.15 Alcohol Ethoxylate (E2.5)

Into a dried 500 ml 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C14,15 Ethoxylate (E2.5) (72.2 g, 0.22 mol) and diethyl ether (150 ml). Chlorosulfonic acid (26.8 g, 0.23 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum is increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (51.8 g, 0.24 mol) and methanol (300ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 94 g of yellow tacky solid, the cat

SO₃ analysis shows the sample is about 91% active. The pH of the sample is about 10.3.

The following two analytical methods for characterizing branching in the present invention surfactant compositions are useful:

1) Separation and Identification of Components in Fatty Alcohols (prior to alkoxylation or after hydrolysis of alcohol sulfate for analytical purposes). The position and length of branching found in the precursor fatty alcohol materials is determined by GC/MS techniques [see: D. J. Harvey, Biomed, Environ. Mass Spectrom (1989). 18(9), 719-23; D. J. Harvey, J. M. Tiffany, J. Chromatogr. (1984), 301(1), 173-87; K. A. Karlsson, B. E. Samuelsson, G. O. Steen, Chem. Phys. Lipids (1973), 11(1), 17-38].

2) Identification of Separated Fatty Alcohol Alkoxy Sulfate Components by MS/MS. The position and length of branching is also determinable by Ion Spray-MS/MS or FAB-MS/MS techniques on previously isolated fatty alcohol sulfate components.

The average total carbon atoms of the branched primary alkyl surfactants herein can be calculated from the hydroxyl value of the precursor fatty alcohol mix or from the hydroxyl value of the alcohols recovered by extraction after hydrolysis of the alcohol sulfate mix according to common procedures, such as outlined in "Bailey's Industrial Oil and Fat Products", Volume 2, Fourth Edition, edited by Daniel Swern, pp. 440-441.

Conventional Surface Cleansing Additive:

The hard surface cleaner composition of the present invention additionally contain a conventional surface cleansing additive. The conventional surface cleansing additive are present from about 0.001% to about 99.9% by weight. Preferably, conventional surface cleansing additive will be present from at least about 0.5%, more preferably, at least about 1%, even more preferably at least about 2%, by weight. Additionally, the conventional surface cleansing additives can also be present at least about 5%, at least about 8% and at least about 10%, by weight but it is more preferable that the conventional surface cleansing additive be present in at least about 2% by weight. Furthermore, the conventional surface cleansing additive will be preferably present in the hard surface composition at preferably at less than about 45%, more preferably less than about 40%, even more preferably less than about 35%, even more preferably less than about 30%, even more preferably less than about 20%, by weight. This conventional surface cleansing additive is selected from the group comprising;

- a) liquid carrier;
- b) co-surfactant;
- c) builder;
- d) co-solvent;
- e) polymeric additive;
- f) pH adjusting material;
- g) hydrotropes; and
- h) mixtures thereof.

The co-surfactant, (b), useful in the present invention can be further selected from the group comprising

- i) anionic;
- ii) nonionic;
- iii) cationic;
- iv) amphoteric;
- v) zwitterionic; and
- vi) mixtures thereof;

The polymeric additives, (e), useful in the present invention can be further selected from the group comprising

- 1) polyalkoxyethylene glycol;
- 2) PVP homopolymers or copolymers thereof;
- 3) polycarboxylate;
- 4) sulfonated polystyrene polymer; and
- 5) mixtures thereof.

a) Liquid Carrier:

The balance of the formula can be water and non-aqueous polar solvents with only minimal cleaning action like methanol, ethanol, isopropanol, ethylene glycol, glycol ethers having a hydrogen bonding parameter of greater than 7.7, propylene glycol, and mixtures thereof, preferably isopropanol. The level of non-aqueous polar solvent is usually greater when more concentrated formulas are prepared. Typically, the level of non-aqueous polar solvent is from about 0.5% to about 40%, preferably from about 1% to about 10%, more preferably from about 2% to about 8% (especially for "dilute" compositions) and the level of aqueous liquid carrier is from about 50% to about 99%, preferably from about 75% to about 95%.

b) Co-surfactant:

The hard surface cleaning compositions according to the present invention may optionally contain co-surfactants, preferably selected from: anionic co-surfactants,

cationic co-surfactants; nonionic co-surfactants; amphoteric co-surfactants; and zwitterionic co-surfactants.

A wide range of these co-surfactants can be used in the hard surface cleaning compositions of the present invention. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these co-surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972. Amphoteric co-surfactants are also described in detail in "Amphoteric Surfactants, Second Edition", E.G. Lomax, Editor (published 1996, by Marcel Dekker, Inc.)

The hard surface cleaning compositions of the present invention will preferably comprise from about 0.001% to about 20%, preferably from about 0.1% to about 10%, by weight of co-surfactants. Selected co-surfactants are further identified as follows.

i) Anionic Co-surfactant:

The optional anionic co-cosurfactant component can comprise as little as 0.001% of the compositions herein when it is present, but typically the compositions will contain from about 0.001% to about 20%, more preferably from about 0.1% to about 10%, even more preferably from about 0.1% to about 5% of anionic cosurfactant, when it is present.

Suitable anionic co-surfactants for use herein include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process).

Alkali metal soaps can be made by direct saponification of fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids derived from various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties.

When the term "coconut" is used herein it refers to fatty acid mixtures which typically have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

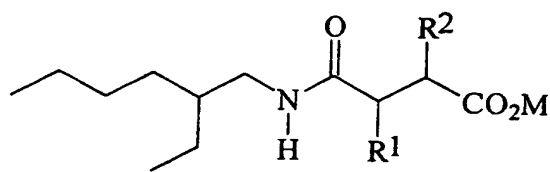
Other suitable anionic co-surfactants for use herein include water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in the molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of these synthetic detergents are the sodium, ammonium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in U.S. Pat. Nos. 2,220,099 and 2,477,383, incorporated herein by reference; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; alkyl benzene sulfates and sulfonates, alkyl ether sulfates, paraffin sulfonates, sulfonates of fatty acids and of fatty acid esters, sulpho succinates, sarcosinates, sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about three moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about four units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts

of fatty acid amide of a methyl taurine in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in U.S. Pat. Nos. 2,486,921, 2,486,922 and 2,396,278, incorporated herein by reference.

The anionic co-surfactants can also be used in the form of their salts, including sodium, potassium, magnesium, ammonium and alkanol/alkyl ammonium salts.

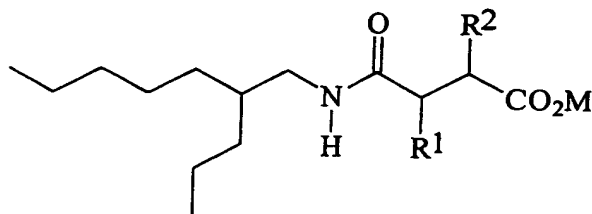
The hard surface cleaning compositions of the present invention may additionally contain one of two sulfosuccinamate co-surfactant. The two possible sulfosuccinamates are:

i) N-2-ethylhexyl sulfosuccinamate:



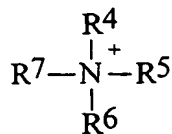
and

ii) N-2-propylheptyl sulfosuccinamate

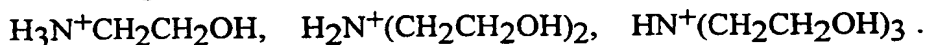


wherein R^1 and R^2 are selected from hydrogen or the moiety $-SO_3M^2$, provided however that R^1 and R^2 are not the same, that is when R^1 is hydrogen, R^2 must be $-SO_3M^2$ and vice versa. M and M^2 are independently selected from hydrogen or a salt forming cation. Three carbon atoms in the above molecule are chiral centers, that is they individually have the capacity to form optical isomers or enantiomers. In addition, when two or more of these chiral carbons are taken together they may form diastereomeric pairs or combinations. For the purposes of the present invention the sulfosuccinamates are drawn such that each chiral center is shown in its racemic form. For the purposes of the present invention all isomeric forms of the sulfosuccinamate are suitable for use in the compositions of the present invention.

M and M^2 may be hydrogen or a salt forming cation depending upon the method of synthesis chosen and the pH of the final hard surface cleaner. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula

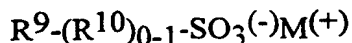


wherein R^4 , R^5 , R^6 and R^7 are independently hydrogen, C_1 - C_{22} alkylene, C_4 - C_{22} branched alkylene, C_1 - C_6 alkanol, C_1 - C_{22} alkenylene, C_4 - C_{22} branched alkenylene, and mixtures thereof. A different salt forming cation may be chosen for the carboxylate moiety ($-\text{CO}_2^-$) than is chosen for the sulfonate moiety ($-\text{SO}_3^-$). Preferred cations are ammonium (R^4 , R^5 , R^6 and R^7 equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R^4 equal to C_1 - C_6 alkanol, R^5 , R^6 and R^7 equal to hydrogen; dialkanol ammonium compounds of the present invention have R^4 and R^5 equal to C_1 - C_6 alkanol, R^6 and R^7 equal to hydrogen; trialkanol ammonium compounds of the present invention have R^4 , R^5 and R^6 equal to C_1 - C_6 alkanol, R^7 equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:



Preferred M and M^2 are hydrogen, sodium, potassium and the C_2 alkanol ammonium salts listed above; most preferred are hydrogen and sodium.

Another group of anionic co-surfactants which can be used in the hard surface cleansing compositions of the present invention have the generic formula:



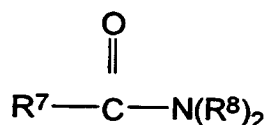
wherein R^9 is a C_6 - C_{20} alkyl chain, preferably a C_8 - C_{16} alkyl chain; R^{10} , when present, is a C_6 - C_{20} alkylene chain, preferably a C_8 - C_{16} alkylene chain, a C_6H_4 phenylene group, or O; and M is the same as before.

Typical of these are the alkyl- and alkylethoxylate- (polyethoxylate) sulfates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxylated) alcohols and alkyl phenols, alkyl phenol sulfonates, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. When the pH is above about 9.5, co-surfactants that are amphoteric at a lower pH are desirable anionic co-cosurfactants. For example, co-surfactants which are C_{12} - C_{18} acylamido alkylene amino alkylene sulfonates, e.g., compounds having the formula $\text{R}-\text{C}(\text{O})-\text{NH}-(\text{C}_2\text{H}_4)-\text{N}(\text{C}_2\text{H}_4\text{OH})-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{M}$ wherein R is an alkyl group containing from about 9 to about 18 carbon atoms and M is a compatible cation are desirable cosurfactants. These co-surfactants are available as Miranol®

CS, OS, JS, etc. The CTFA adopted name for such co-surfactants is cocoamphohydroxypropyl sulfonate.

In general, anionic co-surfactants useful herein contain a hydrophobic group, typically containing an alkyl group in the C₉-C₁₈ range, and, optionally, one or more linking groups such as ether or amido, preferably amido groups. The anionic detergent surfactants can be used in the form of their sodium, potassium or alkanolammonium, e.g., triethanolammonium salts. C₁₂-C₁₈ paraffin-sulfonates and alkyl sulfates are useful anionic co-surfactants in the compositions of the present type.

Some other suitable anionic co-surfactants for use herein in small amounts are one or more of the following: sodium linear C₈-C₁₈ alkyl benzene sulfonate (LAS), particularly C₁₁-C₁₂ LAS; the sodium salt of a coconut alkyl ether sulfate containing 3 moles of ethylene oxide; the adduct of a random secondary alcohol having a range of alkyl chain lengths of from 11 to 15 carbon atoms and an average of 2 to 10 ethylene oxide moieties, several commercially available examples of which are Tergitol® 15-S-3, Tergitol 15-S-5, Tergitol 15-S-7, and Tergitol 15-S-9, all available from Union Carbide Corporation; the sodium and potassium salts of coconut fatty acids (coconut soaps); the condensation product of a straight-chain primary alcohol containing from about 8 carbons to about 16 carbon atoms and having an average carbon chain length of from about 10 to about 12 carbon atoms with from about 4 to about 8 moles of ethylene oxide per mole of alcohol; an amide having one of the preferred formulas:



wherein R⁷ is a straight-chain alkyl group containing from about 7 to about 15 carbon atoms and having an average carbon chain length of from about 9 to about 13 carbon atoms and wherein each R⁸ is a hydroxy alkyl group containing from 1 to about 3 carbon atoms. Another suitable class of surfactants are the fluorocarbon surfactants, examples of which are FC-129®, a potassium fluorinated alkylcarboxylate and FC-170-C®, a mixture of fluorinated alkyl polyoxyethylene ethanols, both available from 3M Corporation, as well as the Zonyl® fluorosurfactants, available from DuPont Corporation. It is understood that mixtures of various anionic co-surfactants can be used.

Other typical optional anionic co-surfactants are the alkyl- and alkyl(polyethoxylate) sulfates, paraffin sulfonates, olefin sulfonates, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well known from the

detergency art. In general, such detergent surfactants contain an alkyl group in the C₉₋₂₂ preferably C₁₀₋₁₈, more preferably C₁₂₋₁₆, range. The anionic co-surfactants can be used in the form of their sodium, potassium or alkanolammonium, e.g., triethanolammonium salts.

A detailed listing of suitable anionic co-surfactants, of the above types, for the hard surface cleaning compositions herein can be found in U.S. Pat. Nos. 4,557,853, and 3,929,678 incorporated by reference hereinbefore. Commercial sources of such surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company, also incorporated hereinbefore by reference.

Anionic co-surfactants suitable for use in the hard surface cleaning compositions include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 0.01 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. The cation M, of the anionic co-surfactant should be chosen such that the anionic co-surfactant component is water soluble. Solubility will depend upon the particular anionic co-surfactants and cations chosen.

Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with between about 0 and about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the hard surface cleaning compositions of the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Other suitable anionic co-surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula $[R_1-SO_3-M]$ where R_1 is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation, as previously described, subject to the same limitations regarding polyvalent metal cations as previously discussed. Examples of such co-surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Still other suitable anionic co-surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Other anionic co-surfactants suitable for use in the hard surface cleaning compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

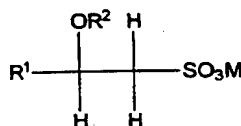
Other suitable anionic co-surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific alpha-olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic co-surfactants suitable for use in the hard surface cleaning compositions are the beta-alkyloxy alkane sulfonates. These compounds have the following formula:



where R¹ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R² is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Some other preferred anionic co-surfactants for use in the hard surface cleaning compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, and sodium dodecyl benzene sulfonate.

ii) nonionic:

The nonionic co-surfactant component can comprise as little as 0.01% of the compositions herein, especially when used with another co-surfactant, but typically the compositions will contain from about 0.5% to about 10%, more preferably from about 1% to about 5%, of nonionic co-surfactant.

It is preferred that, when present, the ratio of nonionic co-surfactant to zwitterionic or amphoteric (non-zwitterionic) co-surfactant, when these co-surfactant are present, is typically from about 1:4 to about 3:1, preferably from about 1:3 to about 2:1, more preferably from about 1:2 to about 1:1.

As an optional component, component (b)(ii), the compositions herein may additionally comprise a hydrophilic nonionic co-surfactant, or mixtures thereof. Suitable hydrophilic nonionic co-surfactants for use herein include alkoxyated alcohols, preferably ethoxylated alcohols. Such co-surfactants can be represented by the formula C_xEO_yH , where C symbolizes the hydrocarbon chain of the alcohol starting material, x represents the length of its hydrocarbon chain. EO represents ethoxy groups and y represents the average degree of ethoxylation, i.e. the average number of moles of ethoxy groups per mole of alcohol. Suitable hydrophilic nonionic co-surfactants for use herein include those where x is of from 9 to 18, preferably 9 to 14, and average y is of from 8 to 30, preferably 10 to 20. Also suitable hydrophilic nonionic co-surfactants are ethoxylated and propoxylated alcohols which can be represented by the formula $C_xPO_yEO_{y'}$, where x is as above, and $(y+y')$ is as y above.

As an optional component, the compositions herein may additionally contain a hydrophobic nonionic co-surfactant (b)(ii), or mixtures thereof. Suitable hydrophobic nonionic co-surfactants for use herein include alkoxyated alcohols, preferably ethoxylated alcohols. Such co-surfactants can be represented by the formula C_xEO_yH , where C symbolizes the hydrocarbon chain of the alcohol starting material, x represents the length of its hydrocarbon chain. EO represents ethoxy groups and y represents the average degree of ethoxylation, i.e. the average number of moles of ethoxy groups per mole of alcohol. Suitable hydrophobic nonionic co-surfactants for use herein include those where x is of from 9 to 18, preferably 9 to 16, and y is of from 2 to 7, preferably 4 to 7. Suitable hydrophobic nonionic co-surfactants also include ethoxylated and propoxylated alcohols which can be represented by the formula $C_xPO_yEO_{y'}$, where x is as above x and where $(y+y')$ is as y above. The compositions herein can comprise mixtures of such hydrophobic nonionics, and when present, the compositions may comprise from 1% to 20%, preferably from 3% to 15% by weight of the total composition of such hydrophobic nonionic co-surfactants, or mixtures thereof.

Another type of suitable nonionic co-surfactants for use herein include a class of compounds which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or

secondary alcohols) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well-known class of nonionic synthetic is made available on the market under the trade name "Pluronic". These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water-insolubility has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole and the liquid character of the products is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic co-surfactants include :

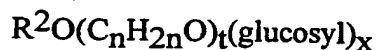
- (i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane;
- (ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000;
- (iii) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms;
- (iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group

ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; the alkyl groups can contain hydroxy substituents; specific examples are dodecyl di(2-hydroxyethyl)amine oxide and tetradecyl dimethyl phosphine oxide.

Also useful as a nonionic co-surfactant are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose, and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions of the preceding saccharide units.

Optionally there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexagluco-sides.

The preferred alkylpolyglycosides have the formula:



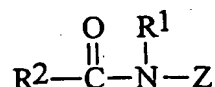
wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon

atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6- position, preferably predominately the 2- position.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use herein. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available PluronicTM co-surfactants, marketed by BASF.

Also suitable for use as nonionic co-surfactants herein are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5000 to about 11000. Examples of this type of nonionic co-surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Other suitable nonionic co-surfactants for use herein include polyhydroxy fatty acid amides of the structural formula :



wherein : R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₁ hydrocarbyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl

or alkenyl, most preferably straight chain C₁₁-C₁₇ alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR')(CHOH)-CH₂OH, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

Additionally R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Suitable nonionic co-surfactants which can be used are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Hard surface cleaning compositions according to the invention can also contain a highly ethoxylated nonionic co-surfactant. The highly ethoxylated nonionic co-surfactants which can be used in the compositions belong to the group according to the formula RO-(CH₂CH₂O)_nH, wherein R is a C₈ to C₂₂ alkyl chain or a C₈ to C₂₈ alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof. Accordingly, one of the preferred nonionic co-surfactants for use in the compositions according to the present invention are those according to the above formula where n is from 11 to 35, more preferably 18 to 35, most preferably 21 to 30. The preferred R chains for use herein are the C₈ to C₂₂ alkyl chains. Suitable chemical processes for preparing the highly ethoxylated nonionic co-

surfactants for use herein have been extensively described in the art. Suitable highly ethoxylated nonionic co-surfactants for use herein are also commercially available, for instance in the series commercialized under the trade name LUTENSOL[®] R from BASF or DOBANOL[®] R from SHELL. A preferred highly ethoxylated alcohol for use herein is LUTENSOL[®] R AO30 (R is a mixture of C₁₃ and C₁₅ alkyl chains, and n is 30). It is also possible to use mixtures of such highly ethoxylated nonionic co-surfactants, with different R groups and different ethoxylation degrees.

Furthermore, the compositions according to the invention can also contain a nonionic co-surfactant system comprising at least a nonionic co-surfactant with an HLB of at least 12, hereinafter referred to as highly hydrophilic co-surfactant and at least a nonionic co-surfactant with an HLB below 10 and at least 4 less than that of said highly hydrophilic co-surfactant, hereinafter referred to as highly hydrophobic co-surfactant.

Suitable nonionic co-surfactants for the implementation of said co-surfactant system are alkoxylated alcohols or alkoxylated phenylalcohols which are commercially available with a variety of alcohol chain lengths and a variety of alkoxylation degrees. By simply varying the length of the chain of the alcohol and/or the degree of alkoxylation, alkoxylated alcohols or alkoxylated phenylalcohols can be obtained with different HLB values. It is to be understood to those ordinarily skilled in the art that the HLB value of any specific compound is available from the literature.

Suitable chemical processes for preparing the highly hydrophilic and highly hydrophobic nonionic co-surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxylated alcohols suitable for use herein is commercially available from various suppliers.

The highly hydrophilic nonionic co-surfactants which can be used in the present invention have an HLB of at least 12, preferably above 14 and most preferably above 15. Those highly hydrophilic nonionic co-surfactants have been found to be particularly efficient for a rapid wetting of typical hard surfaces covered with greasy soils and to provide effective soil suspension.

The highly hydrophobic nonionic co-surfactants which can be used in the present invention have an HLB below 10, preferably below 9 and most preferably below 8.5. Those highly hydrophobic nonionic co-surfactants have been found to provide excellent grease cutting and emulsification properties.

When present, the preferred highly hydrophilic nonionic co-surfactants which can be used in the compositions according to the present invention are co-surfactants having an HLB from 12 to 20 and being according to the formula $RO-(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C₈ to C₂₂ alkyl chain or a C₈ to C₂₈ alkyl benzene chain, and wherein n+m is from 6 to 100 and n is from 0 to 100 and m is from 0 to 100, preferably n+m is from 21 to 50 and, n and m are from 0 to 50, and more preferably n+m is from 21 to 35 and, n and m are from 0 to 35. Throughout this description n and m refer to the average degree of the ethoxylation/propoxylation. The preferred R chains for use herein are the C₈ to C₂₂ alkyl chains. Examples of highly hydrophilic nonionic co-surfactants suitable for use herein are LUTENSOL[®] AO30 (HLB=17; R is a mixture of C₁₃ and C₁₅ alkyl chains, n is 30 and m is 0) commercially available from BASF, CETALOX[®] 50 (HLB= 18 ; R is a mixture of C₁₆ and C₁₈ alkyl chains, n is 50 and m is 0) commercially available from WITCO Alfonic[®] R and 810-60 (HLB=12; R is a mixture of C₈ and C₁₀ alkyl chains, n is 6 and m is 0); and MARLIPAL[®] R 013/400 (HLB= 18; R is a mixture of C₁₂ and C₁₄, n is 40 and m is 0) commercially available from HULS.

When present, the preferred highly hydrophobic nonionic co-surfactants which can be used in the compositions according to the present invention are co-surfactants having an HLB of from 2 to 10 and being according to the formula $RO-(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C₈ to C₂₂ alkyl chain or a C₈ to C₂₈ alkyl benzene chain, and wherein n+m is from 0.5 to 5 and n is from 0 to 5 and m is from 0 to 5, preferably n+m is from 0.5 to 4 and, n and m are from 0 to 4, more preferably n+m is from 1 to 4 and, n and m are from 0 to 4. The preferred R chains for use herein are the C₈ to C₂₂ alkyl chains. Examples of highly hydrophobic nonionic co-surfactants suitable for use herein are DOBANOL[®] R 91-2.5 (HLB= 8.1; R is a mixture of C₉ and C₁₁ alkyl chains, n is 2.5 and m is 0) commercially available from SHELL, LUTENSOL[®] AO3 (HLB=8; R is a mixture of C₁₃ and C₁₅ alkyl chains, n is 3 and m is 0) commercially available from BASF; Neodol 23-3 (HLB=7.9; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 3 and m is 0) and TERGITOL[®] R 25L3 (HLB= 7.7; R is in the range of C₁₂ to C₁₅ alkyl chain length, n is 3 and m is 0) commercially available from UNION CARBIDE.

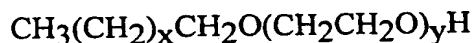
It is possible to use for each category of nonionic co-surfactants (highly hydrophilic or highly hydrophobic) either one of the nonionic co-surfactant belonging to said category or mixtures thereof.

The compositions according to the present invention may contain said highly hydrophilic nonionic co-surfactant in an amount of preferably at least 0.1 %, more

preferably of at least 0.5 %, even more preferably of at least 2 %, and said highly hydrophobic nonionic co-surfactant in an amount of preferably at least 0.1%, more preferably of at least 0.5 %, even more preferably of at least 2 %.

Optionally in the compositions according to the present invention, said highly hydrophilic and highly hydrophobic nonionic co-surfactants, when they are present, may be used in a weight ratio from one to another of from 0.1:1 to 1:0.1, preferably of from 0.2:1 to 1:0.2.

The hard surface cleaning compositions of the present invention may optionally comprise a nonionic co-surfactant having the formula



wherein x is from about 6 to about 12, preferably from about 8 to about 10; y is from about 3.5 to about 10, preferably from about 4 to about 7. For the purposes of the present invention the index y refers to the average degree of ethoxylation obtained when contacting a suitable alcohol with a source of ethyleneoxy moieties, and therefore represents all fractional parts within the range 3.5 to 10.

Nonionic co-surfactants useful herein include any of the well-known nonionic co-surfactants that have an HLB of from about 6 to about 18, preferably from about 8 to about 16, more preferably from about 8 to about 10. High HLB nonionic co-surfactants, when present, have an HLB preferably above about 12, more preferably above about 14, and even more preferably above about 15, and low HLB nonionic co-surfactants, when present, have an HLB of preferably below about 10, more preferably below about 9, and even more preferably below about 8.5. The difference between the high and low HLB values can preferably be at least about 4.

The nonionic co-surfactant can also be a peaked nonionic co-surfactants. A "peaked" nonionic co-surfactant is one in which at least about 70%, more preferably at least about 80%, more preferably about 90%, of the molecules, by weight, contain within two ethoxy groups (moieties) of the average number of ethoxy groups. Peaked nonionic co-surfactants have superior odor as compared to nonionic co-surfactants having a "normal" distribution in which only about 60% of the molecules contain within two ethoxy groups of the average number of ethoxy groups.

The HLB of the peaked short chain nonionic co-surfactants is typically from about 6 to about 18, preferably from about 8 to about 16, more preferably from about 8 to about 10, and, as before, mixed low and high HLB short chain peaked nonionic co-surfactants can, preferably should, differ in HLB by at least about 4. In the typical "peaked" distribution at least about 70%, preferably at least about 80%, and more preferably at least about 90%, but less than about 95%, of the nonionic co-

surfactant contains a number of ethoxy moieties within two of the average number of ethoxy moieties.

Another possible nonionic co-surfactant is either an octyl polyethoxylate, or mixtures of octyl and decyl polyethoxylates with from about 0.1% to about 10%, preferably from about 1% to about 5%, of said octyl polyethoxylate. Another polyethoxylate is a mixture of C₆, C₈, and C₁₀ polyethoxylates containing from about 40% to about 80%, preferably from about 50% to about 70%, by weight ethoxy moieties in a peaked distribution. This latter polyethoxylate is especially desirable when the composition is to be used both at full strength and with dilution.

Typical of the more conventional nonionic co-surfactants useful herein are alkoxyated (especially ethoxylated) alcohols and alkyl phenols, and the like, which are well known from the detergency art. In general, such nonionic co-surfactants contain an alkyl group in the C₆-22, preferably C₆-10, more preferably all C₈ or mixtures of C₈-10, as discussed hereinbefore, and generally contain from about 2.5 to about 12, preferably from about 4 to about 10, more preferably from about 5 to about 8, ethylene oxide groups, to give an HLB of from about 8 to about 16, preferably from about 10 to about 14. Ethoxylated alcohols are especially preferred in the compositions of the present type.

Specific examples of nonionic co-surfactants useful herein include: octyl polyethoxylates (2.5) and (5); decyl polyethoxylates (2.5) and (5); decyl polyethoxylate (6); mixtures of said octyl and decyl polyethoxylates with at least about 10%, preferably at least about 30%, more preferably at least about 50%, of said octyl polyethoxylate; and coconut alkyl polyethoxylate (6.5). Peaked cut nonionic co-surfactants include a C₈-10E₅ in which the approximate distribution of ethoxy groups, by weight, is 0=1.2; 1=0.9; 2=2.4; 3=6.3; 4=14.9; 5=20.9; 6=21.5; 7=16.4; 8=9.4; 9=4.1; 10=1.5; 11=0.5; and 12=0.1 and a C₈-10E₇ in which the approximate distribution of ethoxy groups, by weight, is 0=0.2; 1=0.2; 2=0.5; 3=1.5; 4=6.0; 5=10.2; 6=17.2; 7=20.9; 8=18.9; 9=13.0; 10=7.0; 11=3.0; 12=1.0; 13=0.3; and 14=0.1

A detailed listing of suitable nonionic co-surfactants, of the above types, for the detergent compositions herein can be found in U.S. Pat. No. 4,557,853, Collins, issued Dec. 10, 1985, incorporated by reference herein. Commercial sources of such co-surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company, also incorporated herein by reference.

Other suitable nonionic co-surfactants include those compounds produced by condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Some nonionic co-surfactants useful in the hard surface cleaning compositions include the following:

(1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula $[R^1R^2R^3N \rightarrow O]$ where R^1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R^2 and R^3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula $[RR'R''P \rightarrow O]$ where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety;

(7) alkyl polysaccharide (APS) co-surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which description is incorporated herein by reference, and which discloses APS co-surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and polysaccharide (e.g.,

polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); and

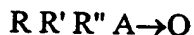
(8) polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ wherein n is from about 5 to about 200, preferably from about 20 to about 100, and R is an aliphatic hydrocarbyl having from about 8 to about 20 carbon atoms.

Other suitable nonionic co-surfactants include other types of amine oxides corresponding to the formula:



wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. The preferred amine oxides are those in which the primary alkyl group has a straight chain in at least most of the molecules, generally at least 70%, preferably at least 90% of the molecules, and the amine oxides which are especially preferred are those in which R contains 10-18 carbons and R' and R'' are both methyl. Exemplary of the preferred amine oxides are the N-hexyldimethylamine oxide, N-octyldimethylamine oxide, N-decyldimethylamine oxide, N-dodecyl dimethylamine oxide, N-tetradecyldimethylamine oxide, N-hexadecyl dimethylamine oxide, N-octadecyldimethylamine oxide, N-eicosyldimethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyl dimethylamine oxide, the corresponding amine oxides in which one or both of the methyl groups are replaced with ethyl or 2-hydroxyethyl groups and mixtures thereof. A most preferred amine oxide for use herein is N-decyldimethylamine oxide.

Other suitable nonionic co-surfactants for the purpose of the invention are other phosphine or sulfoxide co-surfactants of formula:



wherein A is phosphorus or sulfur atom, R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently selected from methyl, ethyl and 2-hydroxyethyl. The arrow in the formula is a conventional representation of a semi-polar bond.

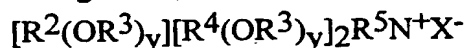
Optionally the nonionic co-surfactant may be a suds controlling nonionic co-surfactant. The formula of these compounds is:

$C_n(PO)_x(EO)_y(PO)_z$, in which C_n represents a hydrophobic group, preferably a hydrocarbon group containing n carbon atoms, n is an integer from about 6 to about 12, preferably from about 6 to about 10; x is an integer from about 1 to about 6, preferably from about 2 to about 4; y is an integer from about 4 to 15, preferably from about 5 to about 12; z is an integer from about 4 to about 25, preferably from about 6 to about 20. These compounds are included in a suds regulating amount to provide good suds control while-maintaining good spotting/filming and rinsing characteristics. The preferable amount of this material, when it is present is from about 0.1% to about 5%, more preferably from about 0.5% to about 2%. These material can be used in addition to other nonionic co-surfactants or in addition to the nonionic form of the mid chain branched surfactant.

Examples of such materials are sold under the trade names Polytergent SLF18 and Polytergent SLF18B.

iii) Cationic:

The hard surface cleaning compositions of the present invention may also optionally contain a cationic co-surfactant. The amount of cationic co-surfactant, when present in the composition can be from about 0.001% to about 10%, preferably from about 0.1% to about 5%, more preferably 0.1% to about 2% by weight. Cationic co-surfactants suitable for use in hard surface cleaning compositions of the present invention include those having a long-chain hydrocarbonyl group. Examples of such cationic co-surfactants include the ammonium co-surfactants such as alkyldimethylammonium halogenides, and those co-surfactants having the formula:

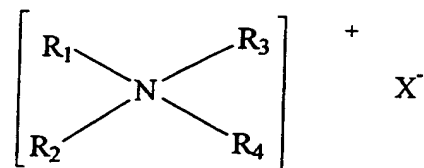


wherein R^2 is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Examples of suitable cationic co-surfactants are described in following documents, all of which are incorporated by reference herein in their entirety: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1997); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology,

New York: Interscience Publishers, 1949; U.S. Patent 3,155,591; U. S. Patent 3,929,678; U. S. Patent 3,959,461 U. S. Patent 4,387,090 and U.S. Patent 4,228,044.

Examples of suitable cationic co-surfactants are those corresponding to the general formula:



wherein R_1 , R_2 , R_3 , and R_4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulfate, and alkylsulfate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R_1 , R_2 , R_3 , and R_4 are independently selected from C1 to about C22 alkyl. Especially preferred are cationic materials containing two long alkyl chains and two short alkyl chains or those containing one long alkyl chain and three short alkyl chains. The long alkyl chains in the compounds described in the previous sentence have from about 12 to about 22 carbon atoms, preferably from about 16 to about 22 carbon atoms, and the short alkyl chains in the compounds described in the previous sentence have from 1 to about 3 carbon atoms, preferably from 1 to about 2 carbon atoms.

iv) Ampohteric:(Non-zwitterionic)

The hard surface cleaning compositions of the present invention may also optionally contain a amphoteric co-surfactant. The amount of amphoteric co-surfactant, when present in the composition can be from about 0.001% to about 10%, preferably from about 0.1% to about 5%, more preferably 0.1% to about 2% by weight. These co-surfactants are similar to the zwitterionic co-surfactants, but the surfactant characteristic of the co-surfactant changes with changes with changes in pH. At one pH it is cationic at another it is anionic.

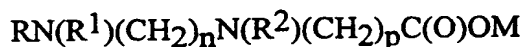
Amphoteric and ampholytic co-surfactants which can be either cationic or anionic depending upon the pH of the system are represented by co-surfactants such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting

dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378, said patents being incorporated herein by reference.

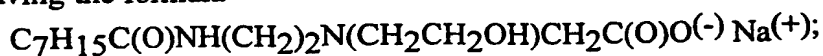
Additional amphoteric co-surfactants and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1997, incorporated herein by reference.

The hard surface cleaning compositions herein may optionally contain from about 0.001% to about 1%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.2%, and even more preferably from about 0.03% to about 0.08%, of C₆₋₁₀ short chain amphocarboxylate co-surfactant. It has been found that these amphocarboxylate, and, especially glycinate, co-surfactants provide good cleaning with superior filming/streaking for hard surface cleaning compositions that are used to clean both glass and/or relatively hard-to-remove soils. Despite the short chain, the detergency is good and the short chains provide improved filming/streaking, even as compared to most of the zwitterionic co-surfactants described hereinafter. Depending upon the level of cleaning desired and/or the amount of hydrophobic material in the composition that needs to be solubilized, one can either use only the amphocarboxylate co-surfactant, or can combine it with other co-surfactant, preferably zwitterionic co-surfactants.

The "amphocarboxylate" co-surfactants herein preferably have the generic formula:



wherein R is a C₆₋₁₀ hydrophobic moiety, typically a fatty acyl moiety containing from about 6 to about 10 carbon atoms which, in combination with the nitrogen atom forms an amido group, R¹ is hydrogen (preferably) or a C₁₋₂ alkyl group, R² is a C₁₋₃ alkyl or, substituted C₁₋₃ alkyl, e.g., hydroxy substituted or carboxy methoxy substituted, preferably, hydroxy ethyl, each n is an integer from 1 to 3, each p is an integer from 1 to 2, preferably 1, and each M is a water-soluble cation, typically an alkali metal, ammonium, and/or alkanolammonium cation. Such co-surfactants are available, for example: from Witco under the trade name Rewoteric AM-V®, having the formula



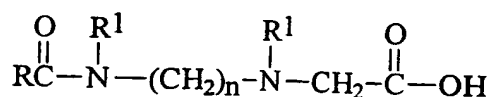
Mona Industries, under the trade name Monateric 1000®, having the formula

$C_7H_{15}C(O)NH(CH_2)_2N(CH_2CH_2OH)CH_2CH_2C(O)O^{(-)}Na^{(+)}$;
and Lonza under the trade name Amphoterger KJ-2®, having the formula

$C_{7,9}H_{15,19}C(O)NH(CH_2)_2N(CH_2CH_2OCH_2C(O)O^{(-)}Na^{(+)})CH_2C(O)O^{(-)}Na^{(+)}$.

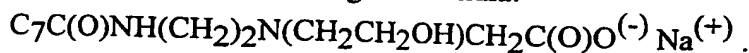
One suitable amphoteric co-surfactant is a C₈₋₁₄ amidoalkylene glycinate co-surfactant. These co-surfactants are essentially cationic at the acid pH.

The glycinate co-surfactants herein preferably have the generic formula, as an acid, of:

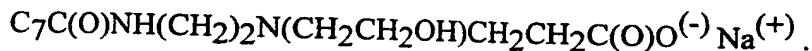


wherein

RC(O) is a C₈₋₁₄, preferably C₈₋₁₀, hydrophobic fatty acyl moiety containing from about 8 to about 14, preferably from about 8 to about 10, carbon atoms which, in combination with the nitrogen atom, forms an amido group, each n is from 1 to 3, and each R¹ is hydrogen (preferably) or a C₁₋₂ alkyl or hydroxy alkyl group. Such co-surfactants are available, e.g., in the salt form, for example, from Sherex under the trade name Rewoteric AM-V, having the formula:



Not all amphoteric co-surfactants are preferred. Longer chain glycinate and similar substituted amino propionates provide a much lower level of cleaning. Such propionates are available as, e.g., salts from Mona Industries, under the trade name Monateric 1000, having the formula:



Cocoyl amido ethyleneamine-N-(hydroxyethyl)-2-hydroxypropyl-1-sulfonate (Miranol CS); C₈₋₁₀ fatty acyl amidoethyleneamine-N-(methyl)ethyl sulfonate; and analogs and homologs thereof, as their water-soluble salts, or acids, are amphoterics that provide good cleaning. Optionally, these amphoterics may be combined with short chain nonionic co-surfactants to minimize sudsing.

Examples of other suitable amphoteric (non-zwitterionic) co-surfactants include:

cocoylamido ethyleneamine-N-(methyl)-acetates;

cocoylamido ethyleneamine-N-(hydroxyethyl)-acetates;

cocoylamido propyl amine-N-(hydroxyethyl)-acetates; and

analogs and homologs thereof, as their water-soluble salts, or acids, are suitable.

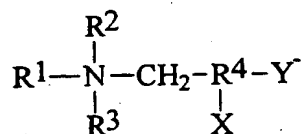
Amphoteric co-surfactants suitable for use in the hard surface cleaning compositions include the derivatives of aliphatic secondary and tertiary amines in

which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

v) Zwitterionic:

The level of zwitterionic co-surfactant, when present in the composition, is typically from about 0.001% to about 10%, preferably from about 0.01% to about 6%, more preferably from about 1% to about 5%.

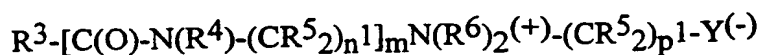
Some suitable zwitterionic co-surfactants which can be used herein comprise the betaine and betaine-like co-surfactants wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference. One of the preferred zwitterionic compounds have the formula



wherein R¹ is an alkyl radical containing from 8 to 22 carbon atoms, R² and R³ contain from 1 to 3 carbon atoms, R⁴ is an alkylene chain containing from 1 to 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R¹, R² and R³ radicals is from 14 to 24 carbon atoms.

Zwitterionic co-surfactants, as mentioned hereinbefore, contain both a cationic group and an anionic group and are in substantial electrical neutrality where the number of anionic charges and cationic charges on the co-surfactant molecule are substantially the same. Zwitterionics, which typically contain both a quaternary ammonium group and an anionic group selected from sulfonate and carboxylate groups are desirable since they maintain their amphoteric character over most of the pH range of interest for cleaning hard surfaces. The sulfonate group is the preferred anionic group.

Preferred zwitterionic co-surfactants have the generic formula:



wherein each Y is preferably a carboxylate (COO^-) or sulfonate (SO_3^-) group, more preferably sulfonate; wherein each R^3 is a hydrocarbon, e.g., an alkyl, or alkylene, group containing from about 8 to about 20, preferably from about 10 to about 18, more preferably from about 12 to about 16 carbon atoms; wherein each (R^4) is either hydrogen, or a short chain alkyl, or substituted alkyl, containing from one to about four carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl; wherein each (R^5) is selected from the group consisting of hydrogen and hydroxy groups with no more than one hydroxy group in any $(\text{CR}^5_2)_p^1$ group; wherein (R^6) is like R^4 except preferably not hydrogen; wherein m is 0 or 1; and wherein each n^1 and p^1 are an integer from 1 to about 4, preferably from 2 to about 3, more preferably about 3. The R^3 groups can be branched, unsaturated, or both and such structures can provide filming/streaking benefits, even when used as part of a mixture with straight chain alkyl R^3 groups. The R^4 groups can also be connected to form ring structures such as imidazoline, pyridine, etc. Preferred hydrocarbonylamidoalkylene sulfobetaine (HASB) co-surfactants wherein $m = 1$ and Y is a sulfonate group provide superior grease soil removal and/or filming/streaking and/or "anti-fogging" and/or perfume solubilization properties. Such hydrocarbonylamidoalkylene sulfobetaines, and, to a lesser extent hydrocarbonylamidoalkylene betaines are excellent for use in hard surface cleaning compositions, especially those formulated for use on both glass and hard-to-remove soils. They are even better when used with monoethanolamine and/or specific beta-amino alkanol as disclosed herein.

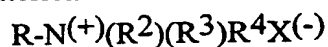
A specific co-surfactant is a C_{10-14} fatty acylamidopropylene(hydroxypropylene)sulfobetaine, e.g., the co-surfactant available from the Witco Company as a 40% active product under the trade name "REWOTERIC AM CAS Sulfobetaine®."

When the zwitterionic co-surfactant is a HASB, it is preferably in the composition from about 0.02% to about 15%, more preferably from about 0.05% to about 10%. The level in the composition is dependent on the eventual level of dilution to make the wash solution. For glass cleaning, the composition, when used full strength, or wash solution containing the composition, should preferably contain from about 0.02% to about 1%, more preferably from about 0.05% to about 0.5%, more preferably from about 0.05% to about 0.25%, of co-surfactant. For removal of difficult to remove soils like grease, the level can, and should be, higher, preferably from about 0.1% to about 10%, more preferably from about 0.25% to about 2%.

Concentrated products will preferably contain from about 0.2% to about 10%, more preferably from about 0.3% to about 5%. It is an advantage of the HASB zwitterionic co-surfactants that compositions containing it can be more readily diluted by consumers since it does not interact with hardness cations as readily as conventional anionic co-surfactants. Zwitterionic co-surfactants are also extremely effective at very low levels, e.g., below about 1%.

Other zwitterionic co-surfactants are set forth at Col. 4 of U.S. Pat. No. 4,287,080, Siklosi, incorporated herein by reference. Another detailed listing of suitable zwitterionic co-surfactants for the compositions herein can be found in U.S. Pat. No. 4,557,853, Collins, issued Dec. 10, 1985, incorporated by reference herein. Commercial sources of such co-surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company, also incorporated herein by reference.

Another preferred zwitterionic co-surfactants is:

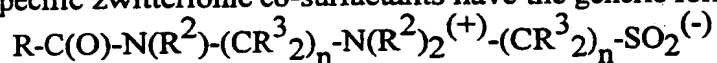


wherein R is a hydrophobic group; R^2 and R^3 are each C_{1-4} alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R^4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from about one to about four carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group.

Preferred hydrophobic groups R are alkyl groups containing from about 8 to about 22, preferably less than about 18, more preferably less than about 16, carbon atoms. The hydrophobic group can contain unsaturation and/or substituents and/or linking groups such as aryl groups, amido groups, ester groups, etc. In general, the simple alkyl groups are preferred for cost and stability reasons.

A specific "simple" zwitterionic co-surfactant is 3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate, available from the Sherex Company under the trade name "Varion HC."

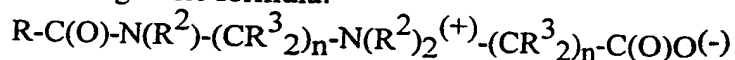
Other specific zwitterionic co-surfactants have the generic formula:



wherein each R is a hydrocarbon, e.g., an alkyl group containing from about 8 up to about 20, preferably up to about 18, more preferably up to about 16 carbon atoms, each (R^2) is either a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to about four carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each (R^3) is

selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to about 4, preferably from 2 to about 3; more preferably about 3, with no more than about one hydroxy group in any $(CR^3)_2$ moiety. The R groups can be branched and/or unsaturated, and such structures can provide spotting/filming benefits, even when used as part of a mixture with straight chain alkyl R groups. The R^2 groups can also be connected to form ring structures. A co-surfactant of this type is a C₁₀₋₁₄ fatty acylamidopropylene(hydroxypropylene)sulfobetaine that is available from the Sherex Company under the trade name "Varion CAS Sulfobetaine".

Other zwitterionic co-surfactants useful, and, surprisingly, preferred, herein include hydrocarbyl, e.g., fatty, amidoalkylenebetaines (hereinafter also referred to as "HAB"). These co-surfactants, which are more cationic at the pH of the composition, have the generic formula:



wherein each R is a hydrocarbon, e.g., an alkyl group containing from about 8 up to about 20, preferably up to about 18, more preferably up to about 16 carbon atoms, each (R^2) is either a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to about four carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each (R^3) is selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to about 4, preferably from 2 to about 3; more preferably about 3, with no more than about one hydroxy group in any $(CR^3)_2$ moiety. The R groups can be branched and/or unsaturated, and such structures can provide spotting/filming benefits, even when used as part of a mixture with straight chain alkyl R groups.

An example of such a co-surfactant is a C₁₀₋₁₄ fatty acylamidopropylenebetaine available from the Miranol Company under the trade name "Mirataine CB."

c) Builders:

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will preferably comprise from about 0.001% to about 10%, more preferably 0.01% to about 7%, even more preferably 0.1% to about 5% by weight of the composition of a builder.

Detergent builders that are efficient for hard surface cleaners and have reduced filming/streaking characteristics at the critical levels can also be present in the compositions of the invention. Addition of specific detergent builders at critical

levels to the present composition further improves cleaning without the problem of filming/streaking that usually occurs when detergent builders are added to hard surface cleaners. There is no need to make a compromise between improved cleaning and acceptable filming/streaking results, which is especially important for hard surface cleaners which are also directed at cleaning glass. These compositions containing these specific additional detergent builders have exceptionally good cleaning properties. They also have exceptionally good shine properties, i.e., when used to clean glossy surfaces, without rinsing, they have much less tendency than, e.g., carbonate built products to leave a dull finish on the surface and filming/streaking.

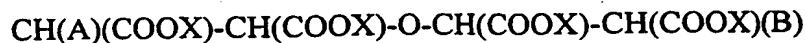
Builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Preferable are builders that have reduced filming/streaking characteristics at the critical levels of the compositions of the present invention.

Suitable builders for use herein include nitrilotriacetates (NTA), polycarboxylates, citrates, water-soluble phosphates such as tri-polyphosphate and sodium ortho-and pyro-phosphates, silicates, ethylene diamine tetraacetate (EDTA), amino-polyphosphonates (DEQUEST), ether carboxylate builders such as in EP-A-286 167, phosphates, iminodiacetic acid derivatives such as described in EP-A-317 542, EP-262 112 and EP-A-399 133, and mixtures thereof. Other suitable optional detergent builders include salts of sodium carboxymethylsuccinic acid, sodium N-(2-hydroxy-propyl)-iminodiacetic acid, and N-diethyleneglycol-N,N-diacetic acid (hereinafter DIDA). The salts are preferably compatible and include ammonium, sodium, potassium and/or alkanolammonium salts. The alkanolammonium salt is preferred as described hereinafter. A one possible builder are the mixtures citric acid/acetate and bicarbonate/carbonate, more preferred bicarbonate/carbonate.

Suitable builders for use herein include polycarboxylates and polyphosphates, and salts thereof.

Suitable and preferred polycarboxylates for use herein are organic polycarboxylates where the highest LogKa, measured at 25°C/0.1M ionic strength is between 3 and 8, wherein the sum of the LogKCa + LogKMg, measured at 25°C/0.1M ionic strength is higher than 4, and wherein $\text{LogKCa} = \text{LogKMg} \pm 2$ units, measured at 25°C/0.1M ionic strength.

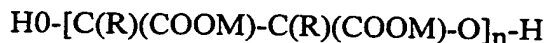
Such suitable and preferred polycarboxylates include citrate and complexes of the formula



wherein A is H or OH; B is H or $-O-CH(COOX)-CH_2(COOX)$; and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydissuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is $-O-CH(COOX)-CH_2(COOX)$, then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly TMS to TDS, these builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Still other ether polycarboxylates suitable for use herein include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulfonic acid, and carboxymethyloxysuccinic acid.

Other useful polycarboxylate builders include the ether hydroxypolycarboxylates represented by the structure :



wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C_{1-4} alkyl or C_{1-4} substituted alkyl (preferably R is hydrogen).

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

Preferred amongst those cyclic compounds are dipicolinic acid and chelidanic acid.

Also suitable polycarboxylates for use herein are mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

Still suitable carboxylate builders herein include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference.

Other suitable carboxylates for use herein are alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic acid builder salts are sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine, tetraacetic acid and nitrilotriacetic acid.

Other suitable polycarboxylates are those also known as alkyliminoacetic builders such as methyl imino diacetic acid, alanine diacetic acid, methyl glycine

diacetic acid, hydroxy propylene imino diacetic acid and other alkyl imino acetic acid builders.

Polycarboxylate detergent builders useful herein, include the builders disclosed in U.S. Pat. No. 4,915,854, Mao et al., issued Apr. 10, 1990, said patent being incorporated herein by reference.

Also suitable for use in the hard surface cleaning compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanediotes and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C5-C20 alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula $R-CH(COOH)CH_2(COOH)$ i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C₁₀-C₂₀ alkyl or alkenyl, preferably C₁₂-C₁₆ or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents. The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts. Specific examples of succinate builders include : laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0 200 263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as

maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Suitable polyphosphonates for use herein are the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates. The most preferred builder for use herein is citrate.

Some suitable carbonate builders for use herein are according to the formula X_2CO_3 or $XHCO_3$ where X is a suitable counterion, typically K^+ , Na^+ or NH_4^+ . Suitable polyphosphates for use herein include compounds of formula $X_aH_bPO_4$, where a and b are integers such that $a+b=3$, and a or b can be 0, or $X_aH_bP_3O_{10}$ where a and b are such that $a+b=5$, and a or b can be 0, and where X is a suitable counterion, particularly K^+ , Na^+ or NH_4^+ .

One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987.

Other useful builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylene-diamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in the compositions and combinations of the present invention.

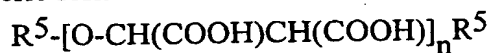
A preferred polycarboxylate builder is iminodisuccinate. Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Other suitable builders include dicarboxylic acids having from about 2 to about 14, preferably from about 2 to about 4, carbon atoms between the carboxyl groups. Specific dicarboxylic detergent builders include succinic, glutaric, and adipic acids, and mixtures thereof. Such acids have a pK_1 of more than about 3 and have

relatively high calcium salt solubilities. Substituted acids having similar properties can also be used.

These dicarboxylic detergent builders provide faster removal of the hard water soils, especially when the pH is between about 2 and about 4.

Other suitable builders that can be used include: citric acid, and, especially, builders having the generic formula:



wherein each R^5 is selected from the group consisting of H and OH and n is a number from about 2 to about 3 on the average. Other preferred detergent builders include those described in the U.S. Pat. No. 5,051,212, Culshaw and Vos, issued Sept. 24, 1991, for "Hard-Surface Cleaning Compositions," said patent being incorporated herein by reference.

In addition to the above detergent builders, other detergent builders that are relatively efficient for hard surface cleaners and/or, preferably, have relatively reduced filming/streaking characteristics include the acid forms of those disclosed in U.S. Pat. No. 4,769,172, Siklosi, issued Sept. 6, 1988, and incorporated herein by reference. Still others include the chelating agents having the formula:



wherein R is selected from the group consisting of:

-CH₂CH₂CH₂OH; -CH₂CH(OH)CH₂; -CH₂CH(OH)CH₂OH; -CH(CH₂OH)₂;
-CH₃; -CH₂CH₂OCH₃; -C(O)-CH₃; -CH₂-C(O)-NH₃; -CH₂CH₂CH₂OCH₃;
-C(CH₂OH)₃; and mixtures thereof; wherein each M is hydrogen.

When it is desired that the hard surface cleaning composition be acidic, i.e. pH < 7, and acidic builder can be used to provide the desired pH in use. However, if necessary, the composition can also contain additional buffering materials to give a pH in use of from about 1 to about 5.5, preferably from about 2 to about 4.5, more preferably from about 2 to about 4. pH is usually measured on the product. The buffer is selected from the group consisting of: mineral acids such as HCl, HNO₃, etc. and organic acids such as acetic, etc., and mixtures thereof. The buffering material in the system is important for spotting/filming. Preferably, the compositions are substantially, or completely free of materials like oxalic acid that are typically used to provide cleaning, but which are not desirable from a safety standpoint in compositions that are to be used in the home, especially when very young children are present.

Divalent Metal ions:

The hard surface cleaning compositions may additionally contain positive divalent ions in amounts so as to saturate the builder present in the composition.

This "saturation" is preferably used in hard surface cleaning compositions when the hard surface to be cleaned is a delicate surface, namely marble or lacquered wood. See copending application Serial No. 08/981,315, Attorneys Docket No CM954M to Procter & Gamble, all of which is incorporated herein by reference. By "saturate", it is meant herein that there should be enough ions to bind substantially all the builder present in the composition, i.e. at least 75% of the builder, preferably at least 80%, most preferably at least 90% or all of the builder. Thus, for a 100% saturation, the ions should be present most preferably in a molar ratio of builder ions to builder of at least X:2, where X is the maximum potential number of negative charges carried per mole of builder. For instance, if said builder is citrate, then said molar ratio should be at least 3:2, because each mole of citrate can carry 3 negative charges. For the purpose of the present invention and the amount of ions needed therein, the form in which the carboxylate or phosphate groups in the builder are present is not critical. In other words, at certain pH values between 6 to 8 where some of the carboxylate or phosphate groups in the builder are in their protonated form, the preferred X:2 ratio still applies.

The ions can be introduced in the compositions in any form. As far as Mg is concerned, MgCl_2 has been found to be commercially attractive. However MgSO_4 , Mg Phosphates and MgNO_3 are also suitable source of Mg ions for the compositions herein. Without wishing to be bound by theory, we speculate that the ions herein somehow prevent the builder from binding with the calcium in the marble, without preventing the builder from performing in the cleaning operation.

Suitable positive divalent ions for use herein include Mg^{2+} , Ba^{2+} , Fe^{2+} , Ca^{2+} , Zn^{2+} and Ni^{2+} . Most Preferred are Mg^{2+} and Ca^{2+} , or mixtures thereof.

d) Co-solvents:

Optionally, the compositions of the present invention further comprise one or more co-solvents. The level of co-solvent, when present in the composition, is typically from about 0.001% to about 30%, preferably from about 0.01% to about 10%, more preferably from about 1% to about 5%. Co-solvents are broadly defined as compounds that are liquid at temperatures of 20°C-25°C and which are not considered to be surfactants. One of the distinguishing features is that co-solvents tend to exist as discrete entities rather than as broad mixtures of compounds. Some co-solvents which are useful in the hard surface cleaning compositions of the present invention contain from about 1 carbon atom to about 35 carbon atoms, and contain contiguous linear, branched or cyclic hydrocarbon moieties of no more than about 8 carbon atoms. Examples of suitable co-solvents for the present invention include, methanol, ethanol, propanol, isopropanol, 2-methyl pyrrolidinone, benzyl

alcohol and morpholine n-oxide. Preferred among these co-solvents are methanol and isopropanol.

The compositions herein may additionally contain an alcohol having a hydrocarbon chain comprising 8 to 18 carbon atoms, preferably 12 to 16. The hydrocarbon chain can be branched or linear, and can be mono, di or polyalcohols.

The co-solvents which can be used herein include all those known to those skilled in the art of hard-surfaces cleaner compositions. Suitable co-solvents for use herein include ethers and diethers having from 4 to 14 carbon atoms, preferably from 6 to 12 carbon atoms, and more preferably from 8 to 10 carbon atoms, glycols or alkoxyated glycols, alkoxyated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxyated aliphatic branched alcohols, alkoxyated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and cycloalkyl hydrocarbons and halohydrocarbons, C6-C16 glycol ethers and mixtures thereof.

Suitable glycols which can be used herein are according to the formula $\text{HO-CR}_1\text{R}_2\text{-OH}$ wherein R1 and R2 are independently H or a C2-C10 saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Suitable glycols to be used herein are dodecaneglycol and/or propanediol.

Suitable alkoxyated glycols which can be used herein are according to the formula $\text{R-(A)}_n\text{-R}_1\text{-OH}$ wherein R is H, OH, a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R1 is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxyated glycols to be used herein are methoxy octadecanol and/or ethoxyethoxyethanol.

Suitable alkoxyated aromatic alcohols which can be used herein are according to the formula $\text{R (A)}_n\text{-OH}$ wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aromatic alcohols are benzoxyethanol and/or benzoxypropanol.

Suitable aromatic alcohols which can be used herein are according to the formula R-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 1 to 15 and more preferably from 1 to 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

Suitable aliphatic branched alcohols which can be used herein are according to the formula R-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12. Particularly suitable aliphatic branched alcohols to be used herein include 2-ethylbutanol and/or 2-methylbutanol.

Suitable alkoxyated aliphatic branched alcohols which can be used herein are according to the formula R (A)_n-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic branched alcohols include 1-methylpropoxyethanol and/or 2-methylbutoxyethanol.

Hydrophobic Co-solvent

Hydrophobic co-solvents are preferably used, when present in the composition, at a level of from about 0.5% to about 30%, more preferably from about 1% to about 15%, even more preferably from about 2% to about 5%.

In order to improve cleaning in liquid compositions, one can use a hydrophobic co-solvent that has cleaning activity. The hydrophobic co-solvents which may be employed in the hard surface cleaning compositions herein can be any of the well-known "degreasing" co-solvents commonly used in, for example, the dry cleaning industry, in the hard surface cleaner industry and the metalworking industry.

A useful definition of such co-solvents can be derived from the solubility parameters as set forth in "The Hoy," a publication of Union Carbide, incorporated herein by reference. The most useful parameter appears to be the hydrogen bonding parameter which is calculated by the formula:

$$\gamma_H = \gamma_T \left[\frac{a-1}{a} \right]^{1/2}$$

wherein γ_H is the hydrogen bonding parameter, a is the aggregation number,

$$(\text{Log } \alpha = 3.39066 \frac{T_b}{T_c} - 0.15848 - \text{Log } \frac{M}{d}), \text{ and}$$

γ_T is the solubility parameter which is obtained from the formula:

$$\gamma_T = \left[\frac{(\Delta H_{25} - RT)d}{M} \right]^{1/2}$$

where ΔH_{25} is the heat of vaporization at 25°C, R is the gas constant (1.987 cal/mole/deg), T is the absolute temperature in °K, T_b is the boiling point in °K, T_c is the critical temperature in °K, d is the density in g/ml, and M is the molecular weight.

For the compositions herein, hydrogen bonding parameters are preferably less than about 7.7, more preferably from about 2 to about 7, or 7.7, and even more preferably from about 3 to about 6. Co-solvents with lower numbers become increasingly difficult to solubilize in the compositions and have a greater tendency to cause a haze on glass. Higher numbers require more co-solvent to provide good greasy/oily soil cleaning.

Many of such co-solvents comprise hydrocarbon or halogenated hydrocarbon moieties of the alkyl or cycloalkyl type, and have a boiling point well above room temperature, i.e., above about 20°C.

The formulator of compositions of the present type will be guided in the selection of cosolvent partly by the need to provide good grease-cutting properties, and partly by aesthetic considerations. For example, kerosene hydrocarbons function quite well for grease cutting in the present compositions, but can be malodorous. Kerosene must be exceptionally clean before it can be used, even in commercial situations. For home use, where malodors would not be tolerated, the formulator would be more likely to select co-solvents which have a relatively pleasant odor, or odors which can be reasonably modified by perfuming.

The C₆-C₉ alkyl aromatic co-solvents, especially the C₆-C₉ alkyl benzenes, preferably octyl benzene, exhibit excellent grease removal properties and have a low, pleasant odor. Likewise, the olefin co-solvents having a boiling point of at least about 100°C, especially alpha-olefins, preferably 1-decene or 1-dodecene, are excellent grease removal co-solvents.

Generically, glycol ethers useful herein have the formula $R^{11}O-(R^{12}O)_mH$ wherein each R^{11} is an alkyl group which contains from about 3 to about 8 carbon atoms, each R^{12} is either ethylene, propylene or butylene, and m^1 is a number from 1 to about 3. The most preferred glycol ethers are selected from the group consisting of monopropyleneglycolmonopropyl ether, dipropyleneglycolmonobutyl ether, monopropyleneglycolmonobutyl ether, ethyleneglycolmonoethyl ether, ethyleneglycolmonobutyl ether, diethyleneglycolmonoethyl ether,

monoethyleneglycolmonohexyl ether, monoethyleneglycolmonobutyl ether, and mixtures thereof. Some other suitable examples include, Ethylene glycol and propylene glycol ethers are commercially available from the Dow Chemical Company under the tradename "Dowanol" and from the Arco Chemical Company under the tradename "Arcosolv". Other suitable co-solvents including mono- and diethylene glycol *n*-hexyl ether are available from the Union Carbide company.

A particularly preferred type of co-solvent for these hard surface cleaner compositions comprises diols having from 6 to about 16 carbon atoms in their molecular structure. Preferred diol co-solvents have a solubility in water of from about 0.1 to about 20 g/100 g of water at 20°C. The diol co-solvents in addition to good grease cutting ability, impart to the compositions an enhanced ability to remove calcium soap soils from surfaces such as bathtub and shower stall walls. These soils are particularly difficult to remove, especially for compositions which do not contain an abrasive. Other co-solvents such as benzyl alcohol, *n*-hexanol, and phthalic acid esters of C₁₋₄ alcohols can also be used.

Co-solvents such as pine oil, orange terpene, benzyl alcohol, *n*-hexanol, phthalic acid esters of C₁₋₄ alcohols, butoxy propanol, Butyl Carbitol® and 1-(2-*n*-butoxy-1-methylethoxy)propane-2-ol (also called butoxy propoxy propanol or dipropylene glycol monobutyl ether), hexyl diglycol (Hexyl Carbitol®), butyl triglycol, diols such as 2,2,4-trimethyl-1,3-pentanediol, and mixtures thereof, can be used. The butoxy-propanol co-solvent should have no more than about 20%, preferably no more than about 10%, more preferably no more than about 7%, of the secondary isomer in which the butoxy group is attached to the secondary atom of the propanol for improved odor.

e) Polymeric additives:

The hard surface cleaning compositions of the present invention may comprise from about 0.001% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.1% to about 5%, and even more preferably from about 0.1% to about 3% of a polymeric additive. Suitable polymeric additives include:

- 1) polyalkoxylene glycol;
- 2) PVP homopolymers or copolymers thereof;
- 3) polycarboxylate;
- 4) sulfonated polystyrene polymer; and
- 5) mixtures thereof.

1) Polyalkoxylene Glycol:

The hard surface cleaning compositions according to the present invention may contain an antiresoiling agent selected from the group consisting of polyalkoxylene glycol, mono- and dicapped polyalkoxylene glycol and a mixture thereof, as defined herein after. The compositions of the present invention may comprise from 0.001% to 20% by weight of the total composition of said antiresoiling agent or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2% by weight, when such an agent is present in the hard surface cleaning composition.

Suitable polyalkoxylene glycols which can be used herein have the following formula $\text{H-O}-(\text{CH}_2-\text{CHR}_2\text{O})_n\text{-H}$.

Suitable monocapped polyalkoxylene glycols which can be used herein have the following formula $\text{R}_1\text{-O}-(\text{CH}_2-\text{CHR}_2\text{O})_n\text{-H}$.

Suitable dicapped polyalkoxylene glycols which can be used herein are according to the formula $\text{R}_1\text{-O}-(\text{CH}_2-\text{CHR}_2\text{O})_n\text{-R}_3$.

In these formulas of polyalkoxylene glycols, mono and dicapped polyalkoxylene glycols, the substituents R_1 and R_3 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms, R_2 is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and n is an integer greater than 0.

Preferably R_1 and R_3 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, preferably from 1 to 16, more preferably from 1 to 8 and most preferably from 1 to 4, or amino bearing linear or branched, substituted or unsubstituted alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8 and most preferably from 1 to 4. Preferably R_2 is hydrogen, or a linear or branched alkyl group, alkenyl group or aryl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8, and most preferably R_2 is methyl, or hydrogen. Preferably n is an integer from 5 to 1000, more preferably from 10 to 100, even more preferably from 20 to 60 and most preferably from 30 to 50.

The preferred polyalkoxylene glycols, mono and dicapped polyalkoxylene glycols which can be used in the present hard surface cleaning compositions have a molecular weight of at least 200, more preferably from 400 to 5000 and most preferably from 800 to 3000.

Suitable monocapped polyalkoxylene glycols which can be used herein include 2-aminopropyl polyethylene glycol (MW 2000), methyl polyethylene glycol (MW 1800) and the like. Such monocapped polyalkoxylene glycols may be commercially available from Hoescht under the polyglycol series or Hunstman under the tradename XTJ®. Preferred polyalkoxylene glycols are polyethylene glycols like polyethylene glycol (MW 2000).

Optionally the antiresoiling agent is a dicapped polyalkoxylene glycol as defined herein or a mixture thereof. Suitable dicapped polyalkoxylene glycols which can be used herein include O,O'-bis(2-aminopropyl)polyethylene glycol (MW 2000), O,O'-bis(2-aminopropyl)polyethylene glycol (MW 400), O,O'-dimethyl polyethylene glycol (MW 2000), dimethyl polyethylene glycol (MW 2000) or mixtures thereof. Preferred dicapped polyalkoxylene glycol for use herein is dimethyl polyethylene glycol (MW 2000). For instance dimethyl polyethylene glycol may be commercially available from Hoescht as the polyglycol series, e.g. PEG DME-2000®, or from Huntsman under the tradename Jeffamine® and XTJ®.

In a preferred embodiment of the present invention wherein the dicapped polyalkoxylene glycol is an amino dicapped polyalkoxylene glycol, it is preferred for cleaning performance reasons to formulate the liquid compositions herein at a pH equal or lower than the pKa of said amino dicapped polyalkoxylene glycol. Indeed, it has been found that the next-time cleaning performance is especially improved at those pHs when the compositions according to the present invention comprise such an amino dicapped polyalkoxylene glycol, as the dicapped polyalkoxylene glycol.

The non-amino dicapped polyalkoxylene glycols as defined herein are pH independent, i.e., the pH of the composition has no influence on the next-time cleaning performance delivered by a composition comprising such a non-amino dicapped polyalkoxylene glycol, as the dicapped polyalkoxylene glycol.

By "amino dicapped polyalkoxylene glycol", it is meant herein a dicapped polyalkoxylene glycol according to the formula $R_1-O-(CH_2-CHR_2O)_n-R_3$, wherein substituents R_1 , R_2 , R_3 and n are as defined herein before, and wherein at least substituent R_1 or R_3 is an amino bearing linear or branched, substituted or unsubstituted hydrocarbon chain of from 1 to 30 carbon atoms.

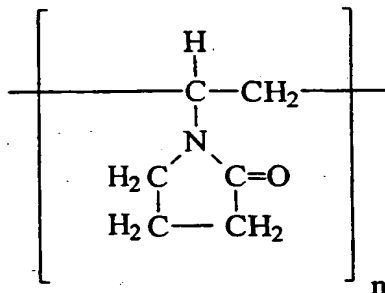
By "non-amino dicapped polyalkoxylene glycol" it is meant herein a dicapped polyalkoxylene glycol according to the formula $R_1-O-(CH_2-CHR_2O)_n-R_3$, wherein substituents R_1 , R_2 , R_3 and n are as defined herein before, and wherein none of the substituents R_1 or R_3 is an amino bearing linear or branched, substituted or unsubstituted hydrocarbon chain of from 1 to 30 carbon atoms.

Although the polyalkoxyene glycols and monocapped polyalkoxyene glycols contribute to the next-time cleaning performance delivered by the compositions herein, the dicapped polyalkoxyene glycols are preferred herein as the next-time cleaning performance associated thereto is further improved. Indeed, it has surprisingly been found that dicapping a polyalkoxyene glycol imparts outstanding improved antiresoiling properties to such a compound, as compared to the corresponding non-capped polyalkoxyene glycol, or non-capped polyalkoxyene glycol of equal molecular weight.

2) PVP homopolymers or copolymers thereof:

The hard surface cleaning compositions according to the present invention may contain a vinylpyrrolidone homopolymer or copolymer or a mixture thereof. The compositions of the present invention comprise from 0.001% to 20% by weight of the total composition of a vinylpyrrolidone homopolymer or copolymer or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2%, when PVP homopolymers or copolymers are present.

Suitable vinylpyrrolidone homopolymers which can be used herein is an homopolymer of N-vinylpyrrolidone having the following repeating monomer:



wherein n (degree of polymerization) is an integer of from 10 to 1,000,000, preferably from 20 to 100,000, and more preferably from 20 to 10,000.

Accordingly, suitable vinylpyrrolidone homopolymers ("PVP") which can be used herein have an average molecular weight of from 1,000 to 100,000,000, preferably from 2,000 to 10,000,000, more preferably from 5,000 to 1,000,000, and most preferably from 50,000 to 500,000.

Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15® (viscosity molecular weight of 10,000), PVP K-30® (average molecular weight of 40,000), PVP K-60® (average molecular weight of 160,000), and PVP K-90® (average molecular weight of 360,000). Other suitable vinylpyrrolidone homopolymers which are commercially available from BASF Cooperation include Sokalan HP 165® and Sokalan HP 12®; vinylpyrrolidone homopolymers known to

persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

Suitable copolymers of vinylpyrrolidone which can be used herein include copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof.

The alkylenically unsaturated monomers of the copolymers herein include unsaturated dicarboxylic acids such as maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole and vinyl acetate. Any of the anhydrides of the unsaturated acids may be employed, for example acrylate, methacrylate. Aromatic monomers like styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

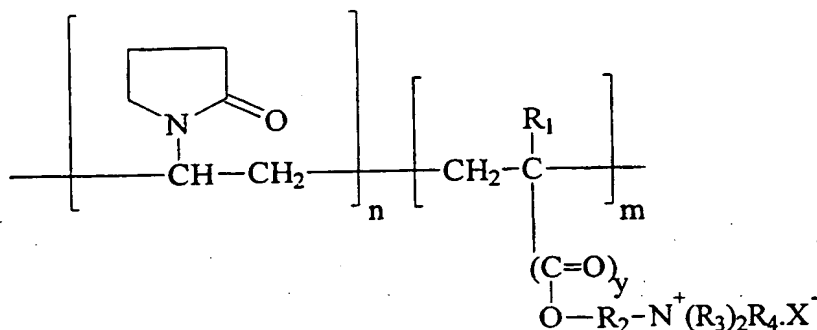
The molecular weight of the copolymer of vinylpyrrolidone is not especially critical so long as the copolymer is water-soluble, has some surface activity and is adsorbed to the hard-surface from the liquid composition or solution (i.e. under dilute usage conditions) comprising it in such a manner as to increase the hydrophilicity of the surface. However, the preferred copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof, have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 200,000.

For example particularly suitable N-vinylimidazole N-vinylpyrrolidone polymers for use herein have an average molecular weight range from 5,000-1,000,000, preferably from 5,000 to 500,000, and more preferably from 10,000 to 200,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol. 113, "Modern Methods of Polymer Characterization".

Such copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers like PVP/vinyl acetate copolymers are commercially available under the trade name Luviskol® series from BASF.

Particular preferred copolymers of vinylpyrrolidone for use in the compositions of the present invention are quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers.

The vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers (quaternised or unquaternised) suitable for use in the compositions of the present invention are according to the following formula:



in which n is between 20 and 99 and preferably between 40 and 90 mol% and m is between 1 and 80 and preferably between 5 and 40 mol%; R_1 represents H or CH_3 ; y denotes 0 or 1; R_2 is $-\text{CH}_2\text{CHOHCH}_2-$ or C_xH_{2x} , in which $x=2$ to 18; R_3 represents a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl, or benzyl; R_4 denotes a lower alkyl group of from 1 to 4 carbon atoms, preferably methyl or ethyl; X^- is chosen from the group consisting of Cl, Br, I, $1/2\text{SO}_4$, HSO_4 and CH_3SO_3 . The polymers can be prepared by the process described in French Pat. Nos. 2,077,143 and 2,393,573.

The preferred quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers suitable for use herein have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 100,000.

Such vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers are commercially available under the name copolymer 845®, Gafquat 734®, or Gafquat 755® from ISP Corporation, New York, NY and Montreal, Canada or from BASF under the tradename Luviquat®.

Most preferred herein is quaternized copolymers of vinyl pyrrolidone and dimethyl aminoethymethacrylate (polyquaternium-11) available from BASF.

3) Polycarboxylate:

The hard surface cleaning composition of the present invention may optionally contain a polycarboxylate polymer. When present the polycarboxylate polymer will be preferably from about 0.001% to about 10%, more preferably from about 0.01% to about 5%, even more preferably about 0.1% to 2.5%, by weight of composition.

Polycarboxylate polymers can be those formed by polymerization of monomers, at least some of which contain carboxylic functionality. Common monomers include acrylic acid, maleic acid, ethylene, vinyl pyrrolidone, methacrylic acid, methacryloylethylbetaine, etc. In general, the polymers should have molecular weights of more than 10,000, preferably more than about 20,000, more preferably more than about 300,000, and even more preferably more than about 400,000. It has also been found that higher molecular weight polymers, e.g.,

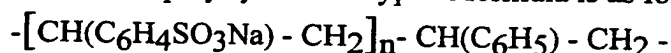
those having molecular weights of more than about 3,000,000, are extremely difficult to formulate and are less effective in providing anti-spotting benefits than lower molecular weight polymers. Accordingly, the molecular weight should normally be, especially for polyacrylates, from about 20,000 to about 3,000,000; preferably from about 20,000 to about 2,500,000; more preferably from about 300,000 to about 2,000,000; and even more preferably from about 400,000 to about 1,500,000.

An advantage for some polycarboxylate polymers is the detergent builder effectiveness of such polymers. Surprisingly, such polymers do not hurt filming/streaking and like other detergent builders, they provide increased cleaning effectiveness on typical, common "hard-to-remove" soils that contain particulate matter.

Some polymers, especially polycarboxylate polymers, thicken the compositions that are aqueous liquids. This can be desirable. However, when the compositions are placed in containers with trigger spray devices, the compositions are desirably not so thick as to require excessive trigger pressure. Typically, the viscosity under shear should be less than about 200 cp, preferably less than about 100 cp, more preferably less than about 50 cp. It can be desirable, however, to have thick compositions to inhibit the flow of the composition off the surface, especially vertical surfaces.

4) Sulfonated Polystyrene Polymer:

Another suitable materials which can be included in to the hard surface cleaning composition of the invention are high molecular weight sulfonated polymers such as sulfonated polystyrene. A typical formula is as follows.



wherein n is a number to give the appropriate molecular weight as disclosed below.

Typical molecular weights are from about 10,000 to about 1,000,000, preferably from about 200,000 to about 700,000.

Examples of suitable materials for use herein include poly(vinyl pyrrolidone/acrylic acid) sold under the name "Acrylidone"® by ISP and poly(acrylic acid) sold under the name "Accumer"® by Rohm & Haas. Other suitable materials include sulfonated polystyrene polymers sold under the name Versaflex® sold by National Starch and Chemical Company, especially Versaflex 7000.

The level of polymer should normally be, when polymer is present in the hard surface cleaning composition, from about 0.01% to about 10%, preferably from about 0.05% to about 0.5%, more preferably from about 0.1% to about 0.3%.

pH Adjusting Material:

The hard surface cleaning compositions of the present invention can be formulated at any pH. That is, the hard surface cleaning compositions of the present invention can have a pH from 0 to 14. Typically, the pH range is selected depending upon the end use of the composition, that is what surface the composition is intended to be used on. Alternatively, the pH can be dependent upon the components present in the composition. That is, glass cleaners will typically have an alkaline pH, i.e. pH greater than 7, preferably a pH from about 8 to about 12, more preferably from about 9 to about 12. All purpose cleaners also typically have an alkaline pH, preferably a pH from about 8 to about 12, more preferably from about 9 to about 12. Bath cleaners or acidic cleaners will have an acidic pH, i.e. pH less than 7, preferably a pH from about 0.5 to about 5.5, more preferably from about 1 to about 5. In bleach containing cleaners the pH of the composition depends upon the bleaching agent used, for example, if hydrogenperoxide is the bleach then the composition is acidic, but if the bleach is a chlorine bleach then the pH will be alkaline. Compositions for use on delicate surfaces, such as marble and lacquered wood, will have a mildly acidic to mildly alkaline pH, preferably the pH is from about 6 to 9, more preferably from about 6.5 to 8 and even more preferably from about 7 to about 7.5. The pH adjusting material, if required, can be then selected with the end use and components present in the composition, to give the composition a pH in the desired range.

The compositions herein may be optionally formulated in a mildly acidic to mildly alkaline range when the composition is designed to clean delicate surfaces. Accordingly, the compositions for use on delicate surfaces preferably have a pH between 6 and 9, more preferably between 6.5 and 8, and most preferably between 7 and 7.5. At lower pH, the composition would damage marble while, at higher pH, it would damage lacquers. Interestingly, even in neutral pH in which the compositions herein can be formulated, damage to marble would be observed in the absence of the saturated citrate. The pH of the compositions herein can be adjusted by any of the means well known to the man skilled in the art, such as addition of NaOH, KOH, MEA, TEA, MDEA, K₂CO₃, Na₂CO₃ and the like, or citric acid, sulphuric acid, nitric acid, hydrochloric acid, maleic acid, acetic acid and the like.

Particularly preferred compositions herein comprise an effective amount of a carbonate of the formula XHCO₃ or, if the builder used is not a phosphate-type builder, a phosphate of the formula X_aH_bPO₄, where a+b=3 and a or b can be 0, X_aH_bP₂O₇ where a+b=4 and a or b can be 0, or X_aH_bP₃O₁₀ where a+b=5 and a or b can be 0, and where X is an alkali metal, particularly K⁺, Na⁺, or NH₄⁺. Indeed, apart from the pH adjusting effect just described, we have found that the presence of

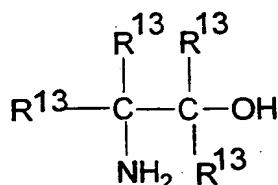
those compounds further improves the safety of the compositions herein to delicate surfaces. Without wishing to be bound by theory, it is believed that the compounds react with the calcium on the surface of marble, to form an insoluble calcium carbonate salt at the marble/solution interface, creating a protective layer. Using these compounds in addition to the saturation technology described hereinabove provides a synergetic effect on delicate surface safety. The amount of these compounds needed in the compositions for use on delicate surfaces can be determined by trial and error, but appears to lie in the range of from 0.05% to 0.4% by weight of the total composition, preferably from 0.05% to 0.1%. Caution needs to be exercised however in that we have observed that too high an amount of XHCO_3 may raise be detrimental to surface safety on lacquered wood.

The liquid compositions herein may be formulated in the full pH range of 0 to 14, preferably 1 to 13. Some of the compositions herein are formulated in a neutral to highly alkaline pH range from 7 to 13, preferably from 9 to 11 and more preferably from 9.5 to 11, dependent upon their use and the components present in the composition. The pH of the compositions herein can be adjusted by any of the means well-known to those skilled in the art such as acidifying agents like organic or inorganic acids, or alkalinizing agents like NaOH, KOH, K_2CO_3 , Na_2CO_3 and the like. Preferred organic acids for use herein have a pK of less than 6. Suitable organic acids are selected from the group consisting of citric acid, lactic acid, glycolic acid, succinic acid, glutaric acid and adipic acid and mixtures thereof. A mixture of said acids may be commercially available from BASF under the trade name Sokalan® DCS.

The compositions according to the present invention may further comprise an alkanolamine, or mixtures thereof, in amounts ranging from 0.1% to 10% by weight of the composition, preferably from 0.1% to 7%, most preferably from 0.1% to 5%. At such levels, the alkanolamine has a buffering effect for alkaline products in the undiluted product, as well as an unexpected boosting effect on the cleaning performance of the diluted compositions. Suitable alkanolamines for use in the compositions according to the present include monoalkanolamines, dialkanolamines, trialkanolamines, alkylalkanolamines, dialkylalkanolamines and alkoxyalkanolamines. Preferred alkanolamines to be used according to the present invention include monoethanolamine, triethanolamine, aminoethylpropanediol, 2-aminomethyl propanol, and ethoxyethanolamine. Particularly preferred are monoethanolamine, triethanolamine and ethoxyethanolamine.

Monoethanolamine and/or beta-alkanolamine, when present in the composition are used at a level of from about 0.05% to about 10%, preferably from about 0.2% to about 5%.

Preferred beta-aminoalkanols have a primary hydroxy group. Suitable beta-aminoalkanols have the formula:



wherein each R^{13} is selected from the group consisting of hydrogen and alkyl groups containing from one to four carbon atoms and the total of carbon atoms in the compound is from three to six, preferably four. The amine group is preferably not attached to a primary carbon atom. More preferably the amine group is attached to a tertiary carbon atom to minimize the reactivity of the amine group. Specific preferred beta-aminoalkanols are 2-amino,1-butanol; 2-amino,2-methylpropanol; and mixtures thereof. The most preferred beta-aminoalkanol is 2-amino,2-methylpropanol since it has the lowest molecular weight of any beta-aminoalkanol which has the amine group attached to a tertiary carbon atom. The beta-aminoalkanols preferably have boiling points below about 175°C . Preferably, the boiling point is within about 5°C of 165°C .

Such beta-aminoalkanols are excellent materials for hard surface cleaning in general and, in the present application, have certain desirable characteristics.

Beta-aminoalkanols, and especially the preferred 2-amino-2-methylpropanol, are surprisingly volatile from cleaned surfaces considering their relatively high molecular weights.

The compositions can optionally contain, either alone or in addition to the preferred alkanolamines, more conventional alkaline buffers such as ammonia; other C_{2-4} alkanolamines; alkali metal hydroxides; silicates; borates; carbonates; and/or bicarbonates. Thus, the buffers that are present usually comprise the preferred monoethanolamine and/or beta-aminoalkanol and additional conventional alkaline material.

g) Hydrotropes:

Hydrotropes are highly preferred optional ingredients. In addition to providing the normal benefits associated with hydrotropes, e.g., phase stability and/or viscosity reduction, hydrotropes can also provide improved suds

characteristics. Specifically, when the zwitterionic and/or amphoteric co-surfactants contain a carboxy group as the anionic group, the hydrotrope can improve both the quantity of suds generated, especially when the product is dispensed from a sprayer or foamer, and, at the same time, reduce the amount of time required for the foam to "break", i.e., the time until the foam has disappeared. Both of these characteristics are valued by consumers, but they are usually considered to be mutually incompatible. The hydrotropes that provide the optimum suds improvements are anionic, especially the benzene and/or alkyl benzene sulfonates. The usual examples of such hydrotropes are the benzene, toluene, xylene, and cumene sulfonates. Typically, these hydrotropes are available as their salts, most commonly the sodium salts. Preferably, the hydrotrope is present in at least about molar equivalency to the zwitterionic and/or amphoteric co-surfactants, when these are present. Preferable levels of hydrotropes, when present, are from about 0.1% to about 5%, more preferably from about 1% to about 3% by weight of composition.

Bleach:

The compositions herein may also comprise a bleaching component. Any bleach known to those skilled in the art may be suitable to be used herein including any peroxygen bleach as well as a chlorine releasing component.

Suitable peroxygen bleaches for use herein include hydrogen peroxide or sources thereof. As used herein a source of hydrogen peroxide refers to any compound which produces active oxygen when said compound is in contact with water. Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, preformed percarboxylic acids, persilicates, persulfates, perborates, organic and inorganic peroxides and/or hydroperoxides.

Suitable chlorine releasing component for use herein is an alkali metal hypochlorite. Advantageously, the composition of the invention are stable in presence of this bleaching component. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

The compositions of the present invention that comprise a peroxygen bleach may further comprise a bleach activator or mixtures thereof. By "bleach activator", it is meant herein a compound which reacts with peroxygen bleach like hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a

method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental-friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally, it provides good building capacity to the composition.

The source of active oxygen according to the present invention acts as an oxidizing agent, it increases the ability of the compositions to remove colored stains and organic stains in general, to destroy malodorous molecules and to kill germs. Suitable sources of active oxygen are hydrogen peroxide or sources thereof. As used herein a hydrogen peroxide source refers to any compound which produces hydrogen peroxide when said compound is in contact with water. Suitable water-soluble inorganic sources of hydrogen peroxide for use herein include persulfate salts (i.e., dipersulfate and monopersulfate salts), persulfuric acid, percarbonates, metal peroxides, perborates and persilicate salts.

In addition, other classes of peroxides can be used as an alternative to hydrogen peroxide and sources thereof or in combination with hydrogen peroxide and sources thereof. Suitable classes include dialkylperoxides, diacylperoxide, performed percarboxylic acids, organic and inorganic peroxides and/or hydroperoxides. Suitable organic peroxides/hydroperoxides include diacyl and dialkyl peroxides/hydroperoxides such as dibenzoyl peroxide, t-butyl hydroperoxide, dilauroyl peroxide, dicumyl peroxide, and mixtures thereof. Suitable preformed peroxyacids for use in the compositions according to the present invention include diperoxydodecandioic acid DPDA, magnesium perphthalic acid, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof.

Persulfate salts, or mixtures thereof, are the preferred sources of active oxygen to be used in the compositions according to the present invention. Preferred persulfate salt to be used herein is the monopersulfate triple salt. One example of monopersulfate salt commercially available is potassium monopersulfate commercialized by Peroxide Chemie GMBH under the trade name Curox®, by Degussa under the trade name Caroat and from Du Pont under the trade name Oxone. Other persulfate salts such as dipersulfate salts commercially available from Peroxide Chemie GMBH can be used in the compositions according to the present invention.

The compositions according to the present invention may optionally comprise up to 30% by weight of the total composition of said bleach, or mixtures thereof, preferably from 0.1% to 20%, more preferably from 0.1% to 10%, and most preferably from 0.1% to 5%.

Chelating Agents

The hard surface cleaning compositions herein may also optionally contain one or more transition metal chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.01% to about 3.0% by weight of such compositions.

Optional Components

The hard surface cleaning compositions of the present invention may further comprise one or more optional components known for use in hard surface cleaning compositions provided that the optional components are physically and chemically

compatible with the essential component described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Concentrations of such optional components typically range from about 0.001% to about 30% by weight of the hard surface cleaning compositions, when present.

Optional components include dyes, diluents, antimicrobial agents, antifungal agents, anti mould agents, antimildew agents, insect repellent, suds suppressors, enzymes, thickeners, thinners, rheology agents (i.e. agents which change or stabilize the rheology of a composition), thixotropic agents, foam boosters, perfumes, preservatives, antioxidants; and aesthetic components such as fragrances, colorings, and the like. This list of optional components is not meant to be exclusive, and other optional components can be used.

Packaging form of the compositions

The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions are preferably packaged in conventional detergent plastic bottles.

In one embodiment the compositions herein may be packaged in manually operated spray dispensing containers, which are usually made of synthetic organic polymeric plastic materials. Accordingly, the present invention also encompasses liquid cleaning compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser or pump spray dispenser.

Indeed, said spray-type dispensers allow to uniformly apply to a relatively large area of a surface to be cleaned the liquid cleaning compositions suitable for use according to the present invention. Such spray-type dispensers are particularly suitable to clean vertical surfaces.

Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunnining et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500® commercially available from Continental Spray International or T 8100® commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced

against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomize the liquid composition, i.e. to help the formation of liquid droplets.

The present invention also comprises a detergent composition containing the branched surfactant mixture, as disclosed herein, in a container in association with instructions to use it with an absorbent structure comprising an effective amount of a superabsorbent material, and, optionally, in a container in a kit comprising the implement, or, at least, a disposable cleaning pad comprising a superabsorbent material.

The container is based on providing the convenience of a cleaning pad, preferably removable and/or disposable, that contains a superabsorbent material and which preferably also provides significant cleaning benefits. The preferred cleaning performance benefits are related to the preferred structural characteristics described below, combined with the ability of the pad to remove solubilized soils. The cleaning pad, as described herein requires the use of the detergent composition containing the branched surfactant mixture to provide optimum performance.

The cleaning pads will preferably have an absorbent capacity when measured under a confining pressure of 0.09 psi after 20 minutes (1200 seconds) (hereafter referred to as "t₁₂₀₀ absorbent capacity") of at least about 10 g deionized water per g of the cleaning pad. The cleaning pads will also preferably, but not necessarily, have a total fluid capacity (of deionized water) of at least about 100 g. Each of the components of the absorbent pad are described in detail.

The absorbent layer is the essential component which serves to retain any fluid and soil absorbed by the cleaning pad during use. While the preferred scrubbing layer, described hereinafter, has some affect on the pad's ability to absorb fluid, the absorbent layer plays the major role in achieving the desired overall absorbency.

From the essential fluid absorbency perspective, the absorbent layer will be capable of removing fluid and soil from any "scrubbing layer" so that the scrubbing layer will have capacity to continually remove soil from the surface.

The absorbent layer will comprise any material that is capable of absorbing and retaining fluid during use. To achieve desired total fluid capacities, it will be preferred to include in the absorbent layer a material having a relatively high capacity (in terms of grams of fluid per gram of absorbent material). As used herein, the term "superabsorbent material" means any absorbent material having a g/g capacity for water of at least about 15 g/g, when measured under a confining pressure of 0.3 psi.

Representative superabsorbent materials include water insoluble, water-swellaable superabsorbent gelling polymers (referred to herein as "superabsorbent gelling polymers") which are well known in the literature. These materials demonstrate very high absorbent capacities for water. The superabsorbent gelling polymers useful in the present invention can have a size, shape and/or morphology varying over a wide range. These polymers can be in the form of particles that do not have a large ratio of greatest dimension to smallest dimension (e.g., granules, flakes, pulverulents, interparticle aggregates, interparticle crosslinked aggregates, and the like) or they can be in the form of fibers, sheets, films, foams, laminates, and the like. The use of superabsorbent gelling polymers in fibrous form provides the benefit of providing enhanced retention of the superabsorbent material, relative to particles, during the cleaning process. While their capacity is generally lower for aqueous-based mixtures, these materials still demonstrate significant absorbent capacity for such mixtures. The patent literature is replete with disclosures of water-swellaable materials. See, for example, U.S. Patent 3,699,103 (Harper et al.), issued June 13, 1972; U.S. Patent 3,770,731 (Harmon), issued June 20, 1972; U.S. Reissue Patent 32,649 (Brandt et al.), reissued April 19, 1989; U.S. Patent 4,834,735 (Alemany et al.), issued May 30, 1989.

Most preferred polymer materials for use in making the superabsorbent gelling polymers are slightly network crosslinked polymers of partially neutralized polyacrylic acids and starch derivatives thereof. Most preferably, the hydrogel-forming absorbent polymers comprise from about 50 to about 95%, preferably about 75%, neutralized, slightly network crosslinked, polyacrylic acid (i.e. poly (sodium acrylate/acrylic acid)). Network crosslinking renders the polymer substantially water-insoluble and, in part, determines the absorptive capacity and extractable polymer content characteristics of the superabsorbent gelling polymers. Processes for network crosslinking these polymers and typical network crosslinking agents are described in greater detail in U.S. Patent 4,076,663.

Other useful superabsorbent materials include hydrophilic polymeric foams, such as those described in commonly assigned copending U.S. patent application Serial No. 08/563,866 (DesMarais et al.), filed November 29, 1995 and U.S. Patent No. 5,387,207 (Dyer et al.), issued February 7, 1995.

The absorbent layer may also consist of or comprise fibrous material. Fibers useful in the present invention include those that are naturally occurring (modified or unmodified), as well as synthetically made fibers.

The fibers useful herein can be hydrophilic, hydrophobic or can be a combination of both hydrophilic and hydrophobic fibers.

Suitable wood pulp fibers can be obtained from well-known chemical processes such as the Kraft and sulfite processes.

Another type of hydrophilic fiber for use in the present invention is chemically stiffened cellulosic fibers. As used herein, the term "chemically stiffened cellulosic fibers" means cellulosic fibers that have been stiffened by chemical means to increase the stiffness of the fibers under both dry and aqueous conditions.

Optional, but Preferred, Scrubbing Layer The scrubbing layer is the portion of the cleaning pad that contacts the soiled surface during cleaning. As such, materials useful as the scrubbing layer must be sufficiently durable that the layer will retain its integrity during the cleaning process. In addition, when the cleaning pad is used in combination with a solution, the scrubbing layer must be capable of absorbing liquids and soils, and relinquishing those liquids and soils to the absorbent layer. This will ensure that the scrubbing layer will continually be able to remove additional material from the surface being cleaned.

In order to provide desired integrity, materials particularly suitable for the scrubbing layer include synthetics such as polyolefins (e.g., polyethylene and polypropylene), polyesters, polyamides, synthetic cellulose (e.g., Rayon®), and blends thereof. Such synthetic materials may be manufactured using known process such as carded, spunbond, meltblown, airlaid, needlepunched and the like.

Optional Attachment Layer The cleaning pads of the present invention can optionally have an attachment layer that allows the pad to be connected to an implement's handle or the support head in preferred implements. The attachment layer will be necessary in those embodiments where the absorbent layer is not suitable for attaching the pad to the support head of the handle. The attachment layer may also function as a means to prevent fluid flow through the top surface (i.e., the handle-contacting surface) of the cleaning pad, and may further provide enhanced integrity of the pad. As with the scrubbing and absorbent layers, the attachment layer may consist of a mono-layer or a multi-layer structure, so long as it meets the above requirements.

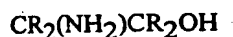
In a preferred embodiment of the present invention, the attachment layer will comprise a surface which is capable of being mechanically attached to the handle's support head by use of known hook and loop technology. In such an embodiment, the attachment layer will comprise at least one surface which is mechanically attachable to hooks that are permanently affixed to the bottom surface of the handle's support head.

Detergent Composition Detergent compositions containing the branched surfactant mixture which are to be used with an implement containing a

superabsorbent material require sufficient detergent to enable the solution to provide cleaning without overloading the superabsorbent material with solution, but cannot have more than about 0.5% detergent surfactant without the performance suffering. Therefore, the level of detergent surfactant should be from about 0.01% to about 0.5%, preferably from about 0.1% to about 0.45%, more preferably from about 0.2% to about 0.45%; the level of hydrophobic materials, including solvent, should be less than about 0.5%, preferably less than about 0.2%, more preferably less than about 0.1%; and the pH should be more than about 9.3.

Preferably the compositions containing the branched surfactant mixture which are to be used in combination with the cleaning implement contain a solvent. Suitable solvents include short chain (e.g., C1-C6) derivatives of oxyethylene glycol and oxypropylene glycol, such as mono- and di-ethylene glycol n-hexyl ether, mono-, di- and tri-propylene glycol n-butyl ether, and the like. The level of hydrophobic solvents, e.g., those having solubilities in water of less than about 3%, more preferably less than about 2%.

Preferably the compositions containing the branched surfactant mixture which are to be used in combination with the cleaning implement contain a builder. Suitable builders include those derived from phosphorous sources, such as orthophosphate and pyrophosphate, and non-phosphorous sources, such as nitrilotriacetic acid, S,S-ethylene diamine disuccinic acid, and the like. Suitable chelants include ethylenediaminetetraacetic acid and citric acid, and the like. Suitable suds suppressors include silicone polymers and linear or branched C10-C18 fatty acids or alcohols. Suitable enzymes include lipases, proteases, amylases and other enzymes known to be useful for catalysis of soil degradation. The total level of such ingredients is low, preferably less than about 0.1%, more preferably less than about 0.05%, to avoid causing filming streaking problems. Preferably, the compositions should be essentially free of materials that cause filming streaking problems. Accordingly, it is desirable to use alkaline materials that do not cause filming and/or streaking for the majority of the buffering. Suitable alkaline buffers are carbonate, bicarbonate, citrate, etc. The preferred alkaline buffers are alkanol amines having the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups containing from one to four carbon atoms and the total of carbon atoms in the compound is from three to six, preferably, 2-amino,2-methylpropanol.

The compositions containing the branched surfactant mixture which are to be used in combination with the cleaning implement preferably contain a polymer. The

level of polymer should be low, e.g., that is from about 0.0001% to about 0.2 %, preferably from about 0.0001% to about 0.1% more preferably from about 0.0005% to about 0.08%, by weight of the composition. This very low level is all that is required to produce a better end result cleaning and higher levels can cause streaking/filming, build up, and/or stickiness.

While not wishing to be limited by theory, two physical properties are considered critical for the polymer: 1) Hydrophilic nature and 2) Shear-thinning ability. The polymer hydrophilicity is important to ensure strippability in-between cleanings to avoid build-up. The shear-thinning characteristic is important in aiding to spread solution out evenly during use and combined with hydrophilic characteristic helps provide leveling effect. By leveling effect we mean minimizing solution de-wetting and molecular aggregation which typically occurs during dry down.. Molecular aggregation leads to visual streaking/filming which is a signal of poor end result cleaning.

Suitable examples of polymers include cellulose materials, e.g., carboxymethylcellulose, hydroxymethylcellulose, etc., and synthetic hydrophilic polymers such as polystyrene sulfonate. More preferred are naturally occurring polymers like gum arabic, pectin, guar gum and xanthan gum. Xanthan gum is particularly preferred. Xanthan gum is disclosed in U.S. Pat. No. 4,788,006, Bolich, issued Nov. 29, 1986, at Col. 5, line 55 through Col. 6, line 2, said patent being incorporated herein by reference. Many synthetic polymers can provide this benefit, especially polymers that contain hydrophilic groups, e.g., carboxylate groups. Other polymers that can provide shear-thinning and hydrophilicity include cationic materials that also contain hydrophilic groups and polymers that contain multiple ether linkages. Cationic materials include cationic sugar and/or starch derivatives.

Preferred polymers are those having higher molecular weights, although molecular weights down to about 5,000 can provide some results. In general, the polymers should have molecular weights of more than about 10,000, preferably more than about 100,000, more preferably more than about 250,000, and even more preferably more than about 500,000. The molecular weight should normally be, from about 10,000 to about 100,000; preferably from about 100,000 to about 1,000,000; more preferably from about 1,000,000 to about 4,000,000; and even more preferably greater than 4,000,000 million.

Examples of suitable materials for use herein include polymers preferably selected from the group consisting of xanthan gums, guar gums, gum arabic, pectin poly(styrene sulfonate), and mixtures thereof of monomers and/or polymers. These polymers can also be used in combination with polymers that do not provide the

benefit or provide the benefit to lesser extent to achieve an improved end result cleaning. The most preferred is xanthan gum.

Cleaning Implements The detergent compositions containing the branched surfactant mixture can be used with an implement for cleaning a surface, the implement preferably comprising:

- a. a handle; and
- b. a removable cleaning pad containing an effective amount of a superabsorbent material, and having a plurality of substantially planar surfaces, wherein each of the substantially planar surfaces contacts the surface being cleaned, more preferably said pad is a removable cleaning pad having a length and a width, the pad comprising
 - i. a scrubbing layer; and
 - ii. an absorbent layer comprising a first layer and a second layer, where the first layer is located between the scrubbing layer and the second layer (i.e., the first layer is below the second layer) and has a smaller width than the second layer.

The Handle The handle of the above cleaning implement can be any material that will facilitate gripping of the cleaning implement. The handle of the cleaning implement will preferably comprise any elongated, durable material that will provide practical cleaning. The length of the handle will be dictated by the end-use of the implement.

The handle will preferably comprise at one end a support head to which the cleaning pad can be releasably attached. To facilitate ease of use, the support head can be pivotably attached to the handle using known joint assemblies. Any suitable means for attaching the cleaning pad to the support head may be utilized, so long as the cleaning pad remains affixed during the cleaning process. Examples of suitable fastening means include clamps, hooks & loops (e.g., Velcro®), and the like. In a preferred embodiment, the support head will comprise hooks on its lower surface that will mechanically attach to the upper layer (preferably a distinct attachment layer) of the absorbent cleaning pad.

A preferred handle, comprising a fluid dispensing means, is depicted in Figure 1 and is fully described in co-pending U.S. Patent Application Serial No. 08/756,774, filed November 15, 1996 by V. S. Ping, et al. (Case 6383), which is incorporated by reference herein. Another preferred handle, which does not contain a fluid dispensing means, is depicted in Figs. 1a and 1b, and is fully described in co-

pending U.S. Patent Application Ser. No. 08/722,731, filed September 23, 1996 by A. J. Irwin (P&G Case 6262), which is incorporated by reference herein.

The Cleaning Pad The cleaning pads described hereinbefore can be used without attachment to a handle, or as part of the above cleaning implement. They may therefore be constructed without the need to be attachable to a handle, i.e., such that they may be used either in combination with the handle or as a stand-alone product. As such, it may be preferred to prepare the pads with an optional attachment layer as described hereinbefore. With the exception of an attachment layer, the pads themselves are as described above.

More information on these cleaning implements including other possible embodiments can be found in PCT Patent Application Serial No. PCT/IB98/00356, filed March 16, 1998 by R. A. Masters, et al. (Case 6555).

Examples

Example III

The following compositions were made by mixing the listed ingredients in the listed proportions. These compositions were used neat to clean marble and dilute to clean lacquered wooden floors. Excellent cleaning and surface safety performance was observed.

	A	B	C	D	E	F	G	H
MBAE	3.0	3.0	5.0	3.2	3.2	3.2	8.0	8.0
Dobanol ® 23-3	1.0	1.0	1.5	1.3	1.3	1.5	3.0	3.5
Empilan	2.0	2.0	2.5	1.9	1.9	2.0	5.0	6.0
KBE21+								
NaPS	2.0	1.5	1.2	1.2	1.0	1.7	3.0	2.5
NaCS	1.2	3.0	2.2	2.0	2.0	1.5	4.0	5.0
MgSO ₄	0.20	0.9	0.30	0.50	1.3	2.0	1.0	3.0
Citrate	0.3	1.0	0.5	0.75	1.8	3.0	1.5	6.0
NaHCO ₃	0.06	0.1	-	0.1	-	0.2	-	-
Na ₂ HPO ₄	-	-	0.1	-	0.3	-	-	-
Na ₂ H ₂ P ₂ O ₇	-	-	-	-	-	-	0.2	0.5
pH	8.0	7.5	7.0	7.25	8.0	7.4	7.5	7.2
Water and Minors	q.s. to 100%							

As used hereinabove:

-MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

-NaPS stands for Na paraffin sulphonate

-NaCS stands for Na cumene sulphonate

-Dobanol® 23-3 is a C12-13 alcohol ethoxylated with an average ethoxylation degree of 3.

-Empilan KBE21 is a C12-14 alcohol ethoxylated with an average ethoxylation degree of 21.

Example IV

	I	J	K	L	M	N
C13-15 EO30	1	-	-	-	-	-
C12-14 EO20	-	-	1	1.7	-	-
C12-14PO3EO7	-	-	-	-	-	2
C12-14 EO10	-	-	-	-	2	-
C10-12 EO10	-	1.5	-	-	-	-
MBAE*	2.8	-	2.4	-	2.4	2.4
C11EO5	-	-	-	5	-	-
C12-14 EO5	4.2	3.0	3.6	-	3.6	3.6
C9-11 EO4	-	3.0	-	-	-	-
C12-OH	-	0.3	-	-	-	-
2-Hexyl decanol	-	-	-	0.4	-	-
2-Butyl octanol	0.3	-	0.3	-	0.3	0.3
MBAS**	-	-	1.0	-	1.0	1.0
MBAES***	1.0	1.3	-	1.5	-	-
Citrate	0.7	1.0	0.7	1.0	0.7	0.7
Na2CO3	0.6	0.7	0.6	0.3	0.6	0.6
	O	P	Q	R	S	
C12-14 EO20	-	1.4	-	2.5	1.8	
C12-14PO3EO7	-	-	-	-	-	
C12-14 EO10	-	-	-	-	-	
C10-12 EO10	2.0	-	1.0	-	-	
C9-11EO5	-	2.0	-	6	4.3	
C11EO5	4.0	-	-	-	-	
C12-14 EO5	-	3.6	4.5	9	6.4	

MBAE*	-	-	3.0	-	-
C12-OH	-	-	-	-	-
2-Hexyl decanol	-	0.3	-	-	-
2-Butyl octanol	0.3	-	0.2	0.5	0.5
MBAS**	1.2	1.5	-	-	1.8
MBAES***	-	-	1.5	2.5	-
Citrate	0.5	1.0	0.5	0.7	0.7
Na ₂ CO ₃	0.3	0.4	0.4	1	1.0

*MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

**MBAS stands for the mid-chain branched alkyl sulfate surfactant according to example II

***MBAES stands for the mid-chain branched alkyl alkoxyate sulfate surfactant according to example I

Example V

The following compositions were made by mixing the listed ingredients in the listed proportions. All proportions are % by weight of the total composition.

Excellent first and next-time cleaning performance and good gloss were delivered to the hard-surfaces cleaned with these compositions both under neat and diluted conditions, e.g. at a dilution level of 50:1 to 200:1 (water:composition).

Compositions (weight%):

	T	U	V	W	X	Y
<u>Nonionic surfactants</u>						
MBAE	2.4	1.9	2.5	-	-	2.5
C12,14 EO5	3.6	2.9	2.5	2.5	-	2.5
C7-9 EO6	-	-	-	-	3.2	-
Dobanol® 23-3	-	-	-	-	1.3	-
AO21	1.0	0.8	4.0	-	1.9	2.0
<u>Anionic surfactants</u>						
NaPS	-	-	-	-	-	-
NaLAS	-	-	-	-	0.9	0.8
NaCS	1.5	2.6	-	2.3	1.2	1.5
MBAS	-	-	-	4.0	0.8	-
Isalchem® AS	0.6	0.6	-	-	-	-

<u>Buffer</u>						
Na ₂ CO ₃	0.6	0.13	0.6	1.0	1.0	0.1
Citrate	0.5	0.56	0.5	-	-	0.6
Caustic	0.3	0.33	0.3	-	-	0.3
<u>Suds control</u>						
Fatty Acid	0.6	0.3	0.5	0.4	0.4	0.5
Isofol 12®	0.3	0.3	-	0.3	0.3	0.3
<u>Polymers</u>						
PEG DME-2000®	0.4	-	0.3	-	-	0.35
Jeffamine® ED-2001	-	0.4	-	-	-	-
Polyglycol AM® 1100	-	-	-	0.5	-	-
PVP K60®	-	0.4	0.6	0.3	-	0.3
PEG (2000)	-	-	-	-	0.5	-
Minors and water	-----	-----	up	to	100%	-----
pH	9.5	7.4	9.5	10.5	10.75	7.5
	Z	AA	BB	CC	DD	EE
<u>Nonionic surfactants</u>						
C 9-11 EO5	-	-	2.5	-	-	-
C12,14 EO5	-	-	-	3.6	-	-
MBAE	3.2	8	-	2.4	3.2	5.0
Dobanol® 23-3	1.3	3.2	2.5	-	1.3	-
AO21	1.9	4.8	-	1.0	1.9	2.0
			2.0			
<u>Anionic surfactants</u>						
NaPS	-	-	-	-	-	-
NaLAS	-	-	-	-	0.9	0.8
NaCS	1.2	3.0	0.8	1.5	1.2	1.5
MBAS	0.8	2.0	1.5	-	0.8	-
Isalchem® AS	-	-	-	0.6	-	-
<u>Buffer</u>						
Na ₂ CO ₃	1.0	2.0	0.2	0.6	1.0	0.2
Citrate	-	-	0.75	0.5	-	0.75
Caustic	-	-	0.5	0.3	-	0.5
<u>Suds control</u>						
Fatty Acid	0.4	0.8	0.4	0.6	0.4	0.4
Isofol 12®	0.3	-	0.3	0.3	0.3	0.3

Polymers

PEG DME-2000®	0.5	0.75	0.5	-	-	-
PVP K60®	-	0.5	0.5	-	-	0.5
Polyquat 11®	0.5	-	-	0.5	0.5	-
MME PEG (2000)	-	-	-	0.5	-	0.5
PEG (2000)	-	-	-	-	0.5	-
Minors and water	----	-- up	to	100%	---	----
pH	10.7	10.75	9.5	9.5	10.75	9.5

PVP K60® is a vinylpyrrolidone homopolymer (average molecular weight of 160,000), commercially available from ISP Corporation, New York, NY and Montreal, Canada.

Polyquat 11® is a quaternized copolymers of vinyl pyrrolidone and dimethyl aminoethylmethacrylate commercially available from BASF.

PEG DME-2000® is dimethyl polyethylene glycol (MW 2000) commercially available from Hoescht.

Jeffamine® ED-2001 is a capped polyethylene glycol commercially available from Huntsman.

PEG (2000) is polyethylene glycol (MW 2000).

MME PEG (2000) is monomethyl ether polyethylene glycol (MW 2000) which was obtained from Fluka Chemie AG.

Isofol 12® is 2-butyl octanol

Dobanol® 23-3 is a C12-C13 EO 3 nonionic surfactant commercially available from SHELL.

C8-AS is octyl sulphate available from Albright and Wilson, under the tradename Empimin® LV 33.

AO21 is a C12-14 EO21 alcohol ethoxylate.

Isalchem® AS is a branched alcohol alkyl sulphate commercially available from Enichem.

MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

MBAS stands for the mid-chain branched alkyl sulfate surfactant according to example II

Example VI

The following compositions were made by mixing the listed ingredients in the listed proportions:

Weight %

Ingredients	FF	GG	HH	II
MBAS*	3	3	3	3
Alcohol ethoxylate 30EO (1)	2	-	-	2
Alcohol ethoxylate 12EO (2)	-	3	-	-
MBAE**	1	-	-	1
Alcohol benzene ethoxylate 10EO (4)	-	-	3	-
Citric acid	2	2	2	3
Butylcarbitol R	4	4	4	7
n-butoxypropoxypropanol	-	-	-	2.5
Triethanolamine	1	1	2	1
water & minors	q.s. to 100%			

Ingredients	Weight %			
	JJ	KK	LL	MM
Sodium paraffin sulfonate	3	-	-	-
MBAS*	-	3	-	-
MBAES***	-	-	3	3
Alcohol ethoxylate 30EO (1)	2	2	1.0	1.0
MBAE**	1	-	3	-
Alcohol ethoxylate 7EO (3)	-	1	-	-
Citric acid	4	3	4	-
Tetrapotassium pyrophosphate	-	-	-	4
Butylcarbitol R	4	4	6	5
n-butoxypropoxypropanol	-	-	-	2
Triethanolamine	-	1	2	-
Monoethanolamine	2	-	-	-
Ethoxyethanolamine	-	-	-	2
water & minors	up to 100%			

*MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

**MBAS stands for the mid-chain branched alkyl sulfate surfactant according to example II

***MBAES stands for the mid-chain branched alkyl alkoxylate sulfate surfactant according to example II

In the examples hereinabove, (1) is a highly ethoxylated nonionic surfactant wherein R is a mixture of C₁₃ and C₁₅ alkyl chains and n is 30. (2) is a highly ethoxylated nonionic surfactant wherein R is a mixture of C₁₃ and C₁₅ alkyl chains and n is 12. (3) is a lower ethoxylated nonionic surfactant wherein n is 7. (4) is a highly ethoxylated nonionic surfactant wherein R is a mixture of C₁₉ and C₂₁ alkyl benzene chains and n is 10.

Compositions FF-MM described hereinabove can be used neat or diluted. In a method according to the present invention, these compositions are diluted in 65 times their weight of water and applied to a hard surface.

Example VII

The following compositions were tested for their cleaning performance when used diluted on greasy soil.

The following compositions were made by mixing the listed ingredients in the listed proportions:

Ingredients	Weight %		
	NN	OO	PP
Sodium paraffin sulfonate	1.0	3	3
Alcohol ethoxylate 7EO	4	-	-
Alcohol ethoxylate 30EO	-	3	2
C12-14 EO21 alcohol ethoxylate	1.0	-	-
MBAE*	5.0	1	2
Sodium Citrate	3	3	3
Butylcarbitol R	4	4	4
Triethanolamine	1	1	1
water & minors	up to 100%		

*MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

EXAMPLE VIII

	QQ	RR	SS	TT	UU
N-2-ethylhexyl sulfosuccinamate	3.0	--	3.0	--	3.0
N-2-propylheptyl sulfosuccinamate	--	3.0	--	3.0	--

C ₁₁ EO ₅	7.0	14.0	14.0	--	--
C ₁₁ EO ₇	--	--	--	7.0	7.0
C ₁₀ EO ₇	7.0	--	--	7.0	7.0
MBAE*	3.0	3.0	3.0	3.0	3.0
Trisodium citrate	1.0	1.0	--	1.0	1.0
Potassium carbonate	0.2	0.2	0.2	0.2	0.2
Triethanol amine	--	--	1.0	--	--
Polycarboxylate co-polymer**	--	--	0.25	--	--
Perfume	1.0	1.0	1.0	1.0	1.0
Alkalinity adjusted to pH	10.5	10.5	7.4	10.5	10.5
Water, salts, fillers	balance	balance	balance	balance	balance

*MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

** SOKALAN CP-9.

EXAMPLE IX

Ingredient	VV	WW	XX	YY	ZZ
IPA ¹	2.0	2.0	2.0	2.0	2.0
BP ²	2.0	2.0	2.0	2.0	2.0
MBAS ³	0.3	0.3	0.2	0.2	0.2
MEA ⁴	0.25	0.25	0.25	0.25	0.25
Cocoamidopropyl-hydroxy-sultaine	0.1	0.1	0.1	0.1	0.1
Capryloamido(carboxy-methoxyethyl)glycinate	0.05	0.05	0.05	0.05	0.05
Polymer Additive	0.5 ⁷	0.2 ⁵	0.2 ⁶	0.2 ⁷	0.2 ⁸
Water and pH adjusted to 9.5	←=====BALANCE=====→				
Balance					

¹Isopropanol

²Butoxypropanol

³MBAS is the mid chain branched alkyl sulfate of example II.

⁴Monoethanolamine

⁵Vinyl pyrrolidone/acrylic acid copolymer (MW about 250,000)

⁶Sodium Polyacrylate (MW about 2,000)

⁷Sodium Polyacrylate (MW about 450,000)

100

⁸Sodium Polyacrylate (MW about 3,000,000)EXAMPLE X

Ingredient	AAA	BBB	CCC
IPA	4.0	4.0	4.0
Ethylene Glycol Monobutyl Ether	2.5	2.5	2.5
MBAS	0.2	0.2	0.2
Sodium Lauryl Sulfate	0.1	0.1	0.1
FC-129 Fluorosurfactant	0.06	0.06	0.06
Sodium Polyacrylate	0.1 ¹⁰	0.2 ⁹	0.2 ¹⁰
Ammonia	0.16	0.16	0.16
Deionized (DI) Water and pH adjusted to 11	◀=====BALANCE=====▶		
Balance			

⁹Sodium Polyacrylate (MW 2,000)¹⁰Sodium Polyacrylate (MW 450,000)EXAMPLE XI

Ingredient	DDD	EEE	FFF
IPA	3.0	3.0	3.0
Ethylene Glycol Monohexyl Ether	0.75	0.75	0.75
MBAS	0.25	0.25	0.25
Sodium Dodecylbenzenesulfonate	0.25	0.25	0.25
Perfume	0.02	0.02	0.2
Sodium Polyacrylate (MW450,000)	0.04	0.2	0.02
Ammonia	0.15	0.15	0.15
pH adjusted to	10.5	11.5	9.5
Deionized (DI) Water to Balance	◀=====BALANCE=====▶		

EXAMPLE XII

Ingredient	GGG	HHH	III
Ethanol	2.8	2.8	2.8
Ethylene Glycol Monobutyl Ether	2.8	2.8	2.8
MBAS	0.3	0.3	0.3
Sodium Alkyl (C ₈ , C ₁₂ , and C ₁₄) Sulfate	0.2	0.2	0.2
Versaflex 7000	---	---	0.1
Versaflex 2004	---	0.1	---
Polymer ⁴	0.1	---	---
Perfume, NaOH (to adjust pH to 9.5), and Soft Water to Balance	◀=====BALANCE=====▶		

Versaflex 2004 and 7000 are sodium sulfonated polystyrenes from National Starch and Chemical Company.

⁴Vinyl pyrrolidone/acrylic acid copolymer (MW about 250,000)

EXAMPLE XIII

<u>Ingredient</u>	<u>Wt. %</u>
3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS) ¹	2.0
Octyl polyethoxylate(2.5) (OPE2.5)	1.1
MBAES ²	2.0
Octyl polyethoxylate(6.0) (OPE6)	2.9
Butoxy Propoxy Propanol (BPP)	5.0
Succinic Acid	10.0
Sodium Cumene Sulfonate (SCS)	4.2
Water, Buffering Agents, and Minors	up to 100
pH	3.0

¹ Varion CAS

² MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example I

EXAMPLE XIV

Ingredient	Wt. %
N-(Coconutamidoethylene)-N-(hydroxyethyl)-glycine ¹	2.0
C ₉₋₁₁ Polyethoxylate (6) (C91E6) ²	2.0
MBAE ³	8.0
Citric Acid	10.0
Butoxy Propoxy Propanol (BPP)	5.0
SCS	1.6
Water, Buffering Agents, and Minors	up to 100
pH	2.97

¹ Rewoteric AM-V² Neodol 91-6³ MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example IIEXAMPLE XV

Ingredient	JJJ	KKK	LLL
3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS) ¹	2.0	-	-
MBAE ²	2.0	2.0	2.0
C ₉₋₁₁ Polyethoxylate (6)(C91E6) ²	2.0	-	-
C ₈₋₁₀ E6	-	2.0	2.0
Cocoamido propyl betaine ³	-	2.0	-
N-(Coconutamidoethylene)-N-(hydroxyethyl)-glycine ⁴	-	-	2.0
BPP	8.0	8.0	8.0
Citric Acid	6.0	6.0	6.0
SCS	1.6	1.6	1.6
Water, Buffering Agents, and Minors	q.s. to 100		
pH	2.97	2.97	2.97

¹ Varion CAS² MBAE stands for the mid-chain branched alkyl polyoxyalkylene surfactant according to example II³ Neodol 91-6⁴ Betaine AMB-15⁵ Rewoteric AM-V

EXAMPLE XVI

Ingredient	MMM	NNN	OOO	PPP
3-(N-dodecyl-N,N- dimethyl)-2-hydroxy- propane-1-sulfonate (DDHPS) ¹	2.0	2.0	2.0	2.0
C ₉₋₁₁ Polyethoxylate (6)(C ₉₁ E ₆) ²	2.0	-	-	-
C ₁₀ E ₆ ³	-	2.0	-	-
MBAE ⁴	3.0	4.0	4.0	5.0
C ₈ E ₆ ⁵	-	-	2.0	-
C ₆ E ₆ ⁶	-	-	-	2.0
BPP	8.0	8.0	8.0	8.0
Citric Acid	6.0	6.0	6.0	6.0
SCS	1.6	1.6	1.6	1.6
pH	2.97	2.98	2.98	3.10
Water, Buffering Agents and Minors	q.s. to 100			

¹ Varion CAS² Neodol 91-6³ Sulfonic L10-6⁴ MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II⁵ Sulfonic L8-6⁶ Sulfonic L6-6

EXAMPLE XVII

Ingredient	QQQ	RRR	SSS	TTT	UUU	VVV	WWW	XXX
3-(N-dodecyl-N,N-dimethyl)2-hydroxypropane-1-sulfonate (DDHPS) ¹	2.0	-	-	-	-	-	-	-
C ₉₋₁₁ Polyethoxylate (6)(C91E6) ²	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
C ₈₋₁₀ E6	-	2.0	2.0	-	-	-	2.0	2.0
MBAE ³	2	1	1	2	3	3	1	1
Lauroamphoglycinate ⁴	-	2.0	-	-	-	-	-	-
Cocamphopropionate ⁵	-	-	-	2.0	-	-	-	-
Tallow Glycinate ⁶	-	-	2.0	-	-	-	-	-
Sodium Lauryliminodipropionate ⁷	-	-	-	-	2.0	-	-	-
Cocamido Propyl Betaine ⁸	-	-	-	-	-	2.0	-	-
Coco Amidopropyl Betaine ⁹	-	-	-	-	-	-	2.0	-
Lauryl Betaine ¹⁰	-	-	-	-	-	-	-	2.0
BPP	8.0	8.0	8.0	8.0	8.0	4.0	4.0	4.0
Citric Acid	6.0	6.0	6.0	6.0	6.0	3.0	3.0	3.0
SCS	3.0	3.0	3.0	3.0	3.0	1.0	1.0	1.0
pH adjusted to Water, Buffering	2.95	3.23	3.05	3.34	3.37	3.5	3.5	3.5
q.s. to 100								

Agents and Minors

¹ Varion CAS² Neodol 91-6³ MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II⁴ Rewoteric AM 2L-35⁵ Rewoteric AM 2CSF⁶ Rewoteric AM TEG⁷ Rewoteric AM LP⁸ Rewoteric AM B14-U⁹ Rewoteric AM B15-U

¹⁰ Rewoteric DML-35

EXAMPLE XVIII

Ingredient	YYY	ZZZ
3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS) ¹	2.0	2.0
C ₉₋₁₁ Polyethoxylate (6)(C91E6) ²	2.0	2.0
MBAE ³	4	1
BPP	8.0	8.0
Citric Acid	6.0	-
Succinic Acid	-	6.0
SCS	3.0	3.0
pH	2.95	3.01
Water, Buffering Agents and Minors	q.s. to 100	

¹ Varion CAS

² Neodol 91-6

³ MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

EXAMPLE XIX

Ingredient	AAAA	BBBB
C ₈₋₁₀ E6	2.0	2.0
Cocoamido propyl betaine ¹	2.0	2.0
MBAE ²	1.0	3.0
BPP	8.0	8.0
Succinic Acid	6.0	6.0
SCS	1.6	1.6
Water, Buffering Agents and Minors	q.s. to 100	
pH	2.00	4.5

¹ Betaine AMB-15

² MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

EXAMPLE XX

Ingredient	CCCC	DDDD	EEEE
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106

3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS) ¹	2.0	-	-
Cocoylamidopropyl Betaine ²	-	1.75	1.75
C9-11 Polyethoxylate (6)(C91E6) ³	2.0	-	-
C8-10 Polyethoxylate (6)(peaked cut C8-10E6) ⁴	-	2.0	2.0
MBAE ⁵	2.0	1.5	1.5
BPP	8.0	6.0	6.0
Citric Acid	6.0	6.0	6.0
SCS	3.0	-	2.0
Water, Buffering Agents and Minors	q.s. to 100		
pH	3.0	3.0	3.0

¹ Varion CAS² Betaine AMB-15-V³ Neodol 91-6⁴ Peaked cut C8-10E6 as described hereinbefore.⁵ MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II**EXAMPLE XXI**

Ingredient	FFFF	GGGG	HHHH
3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS) ¹	2.0	-	-
Cocoylamidopropyl Betaine ²	-	1.75	1.75
C9-11 Polyethoxylate (6)(C91E6) ³	2.0	-	-
C8-10 Polyethoxylate (6)(peaked cut C8-10E6) ⁴	-	2.0	2.0
MBAE ⁵	2.0	1.5	1.5
BPP	8.0	6.0	6.0
Citric Acid	6.0	6.0	6.0
SCS	3.0	-	2.0
Xanthan Gum	0.23	0.23	0.23
Water, Buffering Agents and Minors	q.s. to 100		
pH	3.0	3.0	3.0

¹ Varion CAS² Betaine AMB-15-V³ Neodol 91-6

⁴ Peaked cut C₈₋₁₀E₆ as described hereinbefore.

⁵ MBAE the mid-chain branched alkyl polyoxyalkylene surfactant according to example II

In another embodiment, the surfactant system can be used in cleaning articles such as those of WO 98/24871, published 6/11/98.

EXAMPLE XXII

A detergent composition/solution containing about 0.5% of detergent surfactant, comprising an alcohol ethoxylate detergent surfactant (Neodol 1-5®, available from Shell Chemical Co.) according to example II above; about 0.1%, potassium carbonate; and about 0.5% 2-amino,2-methylpropanol; adjuvants including dyes and perfumes; and the balance deionized water, was applied to a floor surface and removed by an implement as disclosed above (containing an effective amount of sodium polyacrylate, preferably cross-linked sodium polyacrylate, a superabsorbent material) and as exemplified in the drawings. The result is a clean floor.

EXAMPLE XXIII

Ingredient	% Concentration
MBAE (according to example II above)	0.35
MBAS (according to example II)	0.1
Perfume	0.015
K ₂ CO ₃	0.01
1-amino-2-methyl-1-propanol	0.5
Suds suppressor	0.0025
Xanthum gum	0.05
Deionized Water	q.s. to 100%
Ph	adjusted to 7 or higher

* The suds suppressor contains: Polyethylene glycol stearate, Methylated silica Octamethyl cyclotetrasiloxane.

The suds suppressor at an effective level, typically from about 0.0005 to about 0.02, preferably from about 0.001 to about 0.01, more preferably from about 0.002 to about 0.003, provides a technical improvement in spotting and filming, particularly on ceramic surfaces. The reason for this is the grout lines on ceramic create low spots as the mop moves across, generating suds. If too high a level of suds is generated, it can dry down into streaks. Furthermore, consumer research

shows that suds seen on floor during mopping is perceived by some consumers as leading to film/streaking.

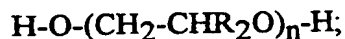
Lowering suds on floor during mopping can provide varying degrees of technical and perceptual benefits for not leaving film/streaks. The degree of benefit depends on the level of suds created and to what degree the level of suds is controlled, particularly during mopping.

Known suds suppressors can be used, but it is highly desirable to use a silicone suds suppressor since they are effective at very low levels and therefore can minimize the total water insoluble material needed while having at least an effective amount of suds suppressor present.

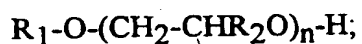
What is claimed is:

1. A hard surface cleaning composition, comprising:

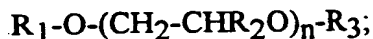
I) from about 0.001% to about 20% by weight of an antiresoiling agent selected from the group comprising
a polyalkoxyethylene glycol according to the formula:



a monocapped polyalkoxyethylene glycol of the formula:



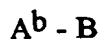
a dicapped polyalkoxyethylene glycol of the formula:



and a mixture thereof, wherein the substituents R_1 and R_3 each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms, R_2 is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and wherein n is an integer greater than 0;

ii) from about 0.1% to about 99.99% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more C_1 - C_3 alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon

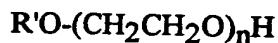
chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})_m\text{OH}$, $(\text{EO/PO})_m\text{OSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5; and
(iii) from about 0.001% to about 20.0%, by weight of a vinylpyrrolidone homopolymer or copolymer.

2. A composition according to any one of claims 1 or 2 wherein said antiresoiling ingredient is a dicapped polyalkoxyethylene glycol or a mixture thereof, and preferably is O,O'-bis(2-aminopropyl)polyethylene glycol (MW 2000), O,O'-bis(2-aminopropyl)polyethylene glycol (MW 400), O,O'-dimethyl polyethylene glycol (MW 2000), dimethyl polyethylene glycol (MW 2000) or a mixture thereof.

3. A hard surface cleaning composition, comprising:
i) from about 0.5% to about 30% by weight of a nonionic surfactant is of the formula



wherein R' is a C_8 to C_{22} alkyl chain or a C_8 to C_{28} alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof; and

ii) from about 0.1% to about 99.5% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

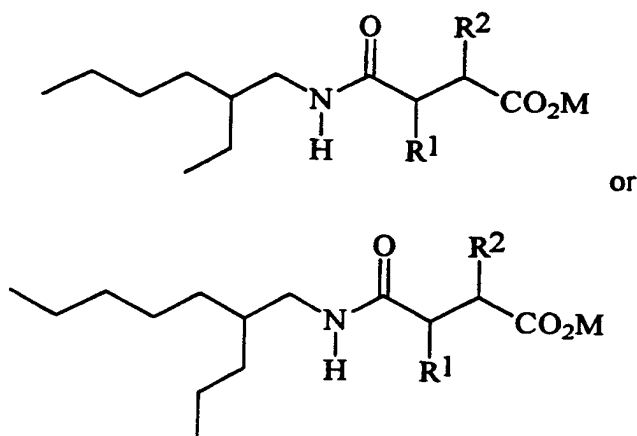
A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $C_1 - C_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(EO/PO)_mOH$, $(EO/PO)_mOSO_3M$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5.

4. A hard surface cleaning composition, comprising:

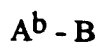
i) from about 0.1% to about 10 % by weight of a sulfosuccinamate selected from the group having the formulas:



wherein R^1 and R^2 are hydrogen or $-SO_3M^2$ provided R^1 does not equal R^2 ; and M and M^2 are independently hydrogen or a salt forming cation;

ii) from about 0.1% to about 99.9% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $C_1 - C_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

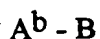
B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})\text{mOH}$, $(\text{EO/PO})\text{mOSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5.

5. A hard surface cleaning composition, comprising:

i) from about 0.1% to about 99.99% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $\text{C}_1 - \text{C}_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

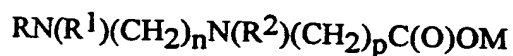
B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})\text{mOH}$, $(\text{EO/PO})\text{mOSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures

thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5;

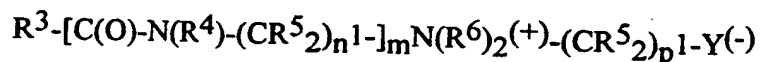
(ii) co-surfactant selected from the group consisting of:

(1) from about 0.001% to about 15% amphocarboxylate co-surfactant having the generic formula :



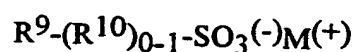
wherein R is a C₆-C₁₀ hydrophobic moiety, including fatty acyl moiety containing from about 6 to about 10 carbon atoms which in combination with the nitrogen atom forms an amido group, R¹ is hydrogen or a C₁₋₂ alkyl group, R² is a C₁₋₂ alkyl, carboxymethoxy ethyl, or hydroxy ethyl, each n is an integer from 1 to 3, each p is an integer from 1 to 2 and M is a water soluble cation selected from alkali metal, ammonium, alkanolammonium, and mixtures thereof cations;

(2) from about 0.02% to about 10% zwitterionic co-surfactant having the generic formula:



wherein each R³ is an alkyl, or alkylene, group containing from about 10 to about 18 carbon atoms, each (R⁴) and (R⁶) is selected from the group consisting of hydrogen, methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, each (R⁵) is selected from the group consisting of hydrogen and hydroxy groups, with no more than about one hydroxy group in any (CR⁵)_p¹ moiety; m is 0 or 1; each n¹ and p¹ is a number from 1 to about 4; and Y is a carboxylate or sulfonate group; and

(3) from about 0.01% to about 2.0% anionic surfactant having the generic formula:

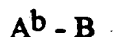


wherein R⁹ is a C₆-C₂₀ alkyl chain; R¹⁰ is a C₆-C₂₀ alkylene chain, a C₆H₄ phenylene group, or O; and M is the same as before; and

- (4) mixtures thereof, and
- (iii) from about 0.5% to about 30%, by weight of hydrophobic solvent, having a hydrogen bonding parameter of from about 2 to about 7.7;
- (iv) alkaline material to provide a pH, measured on the product, of from about 9 to about 12;
- (v) from about 0.01% to about 10% by weight of a substantive polymer that makes glass more hydrophilic, in an effective amount to provide an improvement in spotting/filming after at least three rewetings of the glass, said polymer being selected from the group consisting of polycarboxylate polymer having a molecular weight of from about 10,000 to about 3,000,000 and sulfonated polystyrene polymers having a molecular weight of from about 10,000 to about 1,000,000; and
- (vi) from about 0.1 to about 99.99% by weight of an aqueous liquid carrier.

6. A hard surface cleaning composition, comprising:

- i) from about 0.1% to about 10% by weight of a zwitterionic co-surfactant;
 - ii) from about 0.1% to about 99.99% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture;
- wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $C_1 - C_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1

which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})_m\text{OH}$, $(\text{EO/PO})_m\text{OSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5;

iii) from about 0.1% to about 10%, by weight of a nonionic co-surfactant;

iv) from about 1% to about 20%, by weight of a hydrophobic solvent; and

v) from about 2% to about 14%, by weight of a polycarboxylate builder;

wherein said hard surface cleaning composition has a pH of from about 1 to about 5.5.

7. A detergent composition to be used with an implement containing a pad containing superabsorbent material, comprising:

i) from about 0.0001% to 0.5% by weight of a hydrophobic material; and

ii) from about 0.0001% to 10% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25% and less than about 70% by weight of the branched surfactant mixture; wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $\text{C}_1 - \text{C}_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon

chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})_m\text{OH}$, $(\text{EO/PO})_m\text{OSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5; and said composition has a pH of greater than about 7.

8. A kit comprising an implement containing a pad containing superabsorbent material and a detergent composition comprising

- i) from about 0.0001% to 0.5% by weight of a hydrophobic material; and
- ii) from about 0.0001% to 10% by weight of a surfactant system comprising a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising greater than 25 % and less than about 70% by weight of the branched surfactant mixture; wherein the mid-chain branched surfactant compounds are of the formula:



wherein:

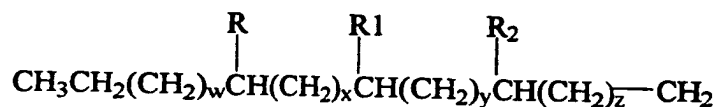
A^b is a hydrophobic moiety having from about 8 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 7 to about 17 carbon atoms, there being one or more $\text{C}_1 - \text{C}_3$ alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position $\omega - 2$ carbon, wherein ω is the terminal carbon;

B is a hydrophilic moiety selected from the group consisting of OSO_3M , $(\text{EO/PO})_m\text{OH}$, $(\text{EO/PO})_m\text{OSO}_3\text{M}$ and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein m is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation;

provided that the average total number of carbon atoms in the A^b moiety in the branched surfactant mixture is within the range of from about 9 to 14.5; and said composition has a pH of greater than about 7.

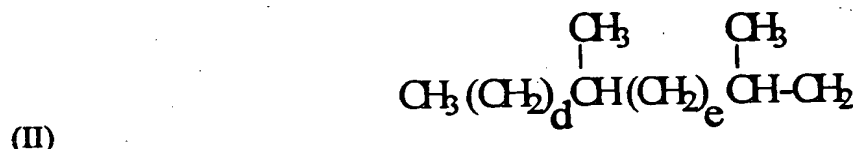
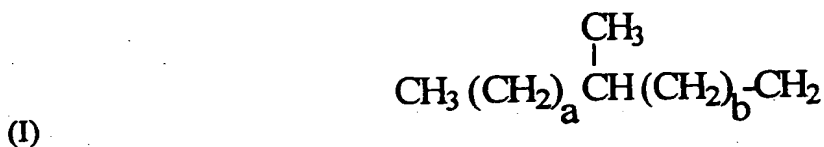
9. The detergent composition either of Claims 7 or 8 further comprising from about 0.0001% to about 0.2% of hydrophilic, shear-thinning polymer that is capable of inhibiting molecular aggregation of surfactant solution on floors during the dry-down process.

10. The hard surface cleaning compositions according to any one of claims 1 to 9 comprising alkyl chain, mid-chain branched surfactant compounds of the above formula wherein the A^b moiety is a branched alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched alkyl moiety of this formula, including the R, R^1 , and R^2 branching, is from 9 to 17; R, R^1 , and R^2 are each independently selected from hydrogen and C_1 - C_3 alkyl, preferably methyl, provided R, R^1 , and R^2 are not all hydrogen and, when z is 0, at least R or R^1 is not hydrogen; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10 and $w + x + y + z$ is from 2 to 10.

11. The hard surface cleaning composition according to any one of claims 1 to 9 –
 wherein the A^b moiety of the mid-chain branched surfactant compound is a branched
 alkyl moiety having a formula selected from the group consisting of:



and mixtures thereof;

wherein a, b, d, and e are integers, a+b is from 5 to 13, d+e is from 3 to 11; and
 when a + b = 5, a is an integer from 2 to 4 and b is an integer from 1 to 3;
 when a + b = 6, a is an integer from 2 to 5 and b is an integer from 1 to 4;
 when a + b = 7, a is an integer from 2 to 6 and b is an integer from 1 to 5;
 when a + b = 8, a is an integer from 2 to 7 and b is an integer from 1 to 6;
 when a + b = 9, a is an integer from 2 to 8 and b is an integer from 1 to 7;
 when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
 when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
 when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
 when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
 when d + e = 3, d is the integer 2 and e is the integer 1;
 when d + e = 4, d is an integer from 2 to 3 and e is an integer from 1 to 2;
 when d + e = 5, d is an integer from 2 to 4 and e is an integer from 1 to 3;
 when d + e = 6, d is an integer from 2 to 5 and e is an integer from 1 to 4;
 when d + e = 7, d is an integer from 2 to 6 and e is an integer from 1 to 5;
 when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;
 when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;
 when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8.
 when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9.

12. A method of cleaning a hard surface, said method comprises applying an effective amount of the composition according to any one of claims 1 to 11 to a hard surface in need of cleaning.

13. A method of cleaning a hard surface, said method comprises applying a diluted aqueous solution of the composition according to any one of claims 1 to 11 to a hard surface in need of cleaning.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 98/21615

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37 C11D3/00 C11D17/04 C11D1/83 C11D1/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 97 38956 A (CONNOR DANIEL STEDMAN ; PROCTER & GAMBLE (US)) 23 October 1997 see page 2, line 31 - page 3, line 13; claims 1-8; example III see page 6, line 26 - line 31 see page 7, line 29 - line 34 ---	3,10,11
P,A	EP 0 859 045 A (PROCTER & GAMBLE) 19 August 1998 see claims 1,4,16; examples A,B,J ---	1,2
A	WO 97 01521 A (SASTECH PTY LTD ; SASOL CHEMICALS EUROP LTD (GB); BETTS MARK JUSTIN) 16 January 1997 cited in the application see example 13 --- -/-	1,10,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

26 January 1999

Date of mailing of the international search report

17/02/1999

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/21615

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>VARADARJA R ET AL: "RELATIONSHIPS BETWEEN DYNAMIC CONTACT ANGLE AND DYNAMIC SURFACE TENSION PROPERTIES FOR LIANER AND BRANCHED ETHOXYLATE, ETHOXYLSULFATE, AND SULFATE SURFACTANTS"</p> <p>JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 147, no. 2, December 1991, pages 403-406, XP000602370</p> <p>cited in the application</p> <p style="text-align: center;">---</p>	
A	<p>VARADARAJ R ET AL: "RELATIONSHIP BETWEEN FUNDAMENTAL INTERFACIAL PROPERTIES AND FOAMING IN LINEAR AND BRANCHED SULFATE, ETHOXYLSULFATE, AND ETHOXYLATE SURFACTANTS"</p> <p>JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 140, no. 1, November 1990, pages 31-34, XP002036586</p> <p>cited in the application</p> <p style="text-align: center;">---</p>	
A	<p>WO 96 04358 A (PROCTER & GAMBLE)</p> <p>15 February 1996</p> <p>see claims 1-11; example IV</p> <p style="text-align: center;">---</p>	5,12,13
A	<p>WO 97 29084 A (PROCTER & GAMBLE)</p> <p>14 August 1997</p> <p>see claims 1-7</p> <p style="text-align: center;">---</p>	4
A	<p>EP 0 357 496 A (COLGATE PALMOLIVE CO)</p> <p>7 March 1990</p> <p>see page 3, line 31 - line 41; claims</p> <p style="text-align: center;">---</p>	8
P,A	<p>WO 98 11813 A (PROCTER & GAMBLE)</p> <p>26 March 1998</p> <p>see page 19, paragraph 3 - page 20, paragraph 2</p> <p style="text-align: center;">-----</p>	8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21615

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